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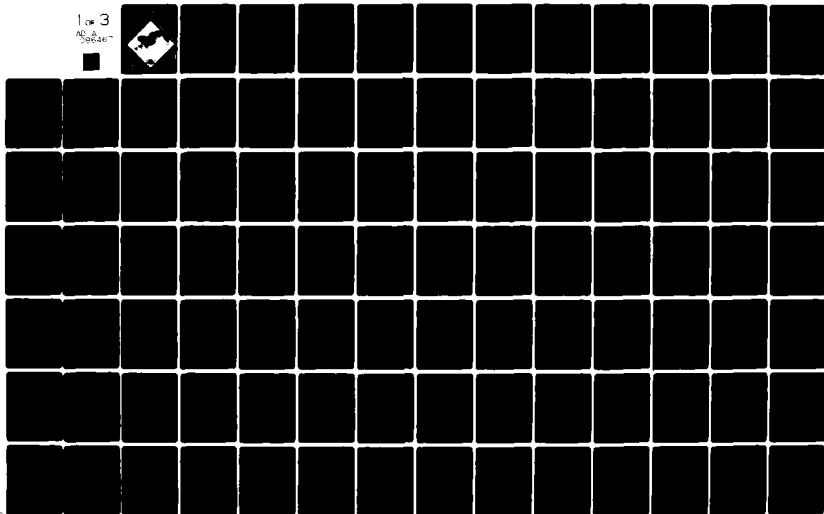
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INSTRUMENTATION FOR DETECTING
HAZARDOUS MATERIALS

June 1980

By: Gerard J. Gross
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For: Federal Emergency Management Agency
Washington, D.C. 20472

Contract # DCPA01-79-C-0305
Work Unit 2533-B

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no instrument exists now in a form ready to use for the role studied here, several types show promise for future development: a remote passive IR absorption instrument, a non-remote dispersive IR analyzer, and a non-remote portable gas chromatograph/mass spectrometer. A number of instrument types for purposes other than primary identification are also reviewed and comments made on application and future development. An extensive list of references on material sensing technology is included.

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Foreword

This report documents the work performed under Contract No. DCPA01-79-C-0305 between June 1979 and June 1980. The work was sponsored by the Office of Mitigation and Research of the Federal Emergency Management Agency (FEMA). Special thanks are due to James W. Kerr for his guidance of this work as the Contracting Officer's Technical Representative (COTR).

The authors of this report are indebted to the many individuals both in government and private industry who provided essential information for the report. Researchers have been generous of their time in discussing the progress of their work, and manufacturers of commercial instruments have been cooperative in providing data on their products. In particular, appreciation is expressed to people from the following groups for their help and generosity in private meetings or lengthy telephone conversations: Chemical Systems Laboratory, Aberdeen Proving Ground; NASA Langley; NASA Technical Utilization Program, Washington, DC; Cal Tech Jet Propulsion Laboratory; Air Force Geophysical Labs, Hanscomb Field, MA; National Bureau of Standards; U.S. Department of Transportation; and EPA Oil and Hazardous Material Spills Branch, Edison, NJ.

The authors also wish to thank the following LOCUS personnel for their contributions to this work: Larry Claypool for help in compiling hazard data on materials; Mary Farmer for typing the original drafts; and the entire LOCUS Publications staff for their expert and timely help in preparing the final copy for the report.

The mention of a specific company or company product in this report is not intended as an official endorsement of that company or its products. Information is provided to present factual data and to allow a comparison between instruments and techniques.

References in this report are numbered, in parentheses, consecutively according to the order of their first appearance in the report, regardless of section number.

1.0 EXECUTIVE SUMMARY

1.1 Purpose and Scope

The purpose of this study has been to evaluate the state of material sensing technology and to analyze its relevance to FEMA missions in the area of hazardous material emergencies. For accomplishing this purpose, the following tasks were performed:

- A list of hazardous materials most likely to be encountered in FEMA emergency missions was compiled, along with pertinent data on these materials.
- An extensive survey of existing instruments and those under development was conducted; and their potential for hazardous material detection was evaluated.
- The requirements for future development of promising systems were determined.

In this study, emphasis has been placed on instruments which would be portable, easy to use, and suitable for the first emergency group to arrive at the scene of an accident. Within this emphasis, additional emphasis was given to remote instruments over those for which a sample of the material must be taken. Nevertheless, because of the number of direct-sampling instruments, a large portion of the report is devoted to these types. Though the study concentrated on instruments for immediate response, comments on the applicability of some systems to intermediate, and late-time response, are made where appropriate.

The emphasis has also been placed on instruments which could identify, out of a large number of possibilities, an unknown hazardous material. Less detail has been devoted to instruments applicable to limited numbers of materials or to functions other than detection and identification of unknowns.

1.2 List of Materials

Table 1.1 presents the names of the hazardous materials which were compiled to serve as the "target" list for the

Table 1.1 - Selected List of Hazardous Materials

GROUP I A

MATERIALS AMONG THE TOP 50 CHEMICALS PRODUCED
AND WHICH SHOW A SIGNIFICANT HAZARD

Sulfuric Acid	Propylene	Xylene	
Oxygen	Benzene	Hydrochloric Acid	Cyclohexane
Ammonia	Ethylene Dichloride	Ethylene Oxide	Acetone
Ethylene	Toluene	Ethylene Glycol	Propylene Oxide
Chlorine	Ethylbenzene	Ammonium Sulfate	Acrylonitrile
Sodium Hydroxide	Vinyl Chloride	Butadiene	Isopropyl Alcohol
Phosphoric Acid	Styrene	Cumene	Vinyl Acetate
Nitric Acid	Formaldehyde	Acetic Acid	Acetic Anhydride
Ammonium Nitrate	Methanol	Phenol	Ethanol

GROUP I B

PETROCHEMICAL OR OTHER FLAMMABLE PRODUCTS KNOWN TO BE SHIPPED
IN LARGE QUANTITIES AND HAVING A HIGH FLAMMABILITY RATING

Gasoline	Propane	Isobutane	Heptane
Kerosene & Jet Fuels	Butane	Pentane	Octane
Fuel Oils	Isopentane	Hexane	Natural Gas
Ethane			Acetylene

GROUP II

MATERIALS IN DEPARTMENT OF TRANSPORTATION'S SELECTED HAZARDOUS
MATERIALS GUIDE, AND WHICH ARE NOT ALREADY IN GROUP I

Acrolein	Epichlorohydrin	Hydrogen Fluoride	Methyl Ethyl Ether
Boron Trifluoride	Ethyl Chloride	Hydrogen Sulfide	Methyl Mercaptan
Bromine	Ethyleneimine	Methane	Nitrogen Tetroxide
Carbon Disulfide	Fluorine	Methylamines	Phosgene
Dimethyl Ether	Hydrogen	Methyl Bromide	Phosphorus Trichloride
Dimethyl Sulfate	Hydrogen Cyanide	Methyl Chloride	Sulfur Dioxide
	Titanium Tetrachloride		

GROUP III

MATERIALS PRODUCED IN QUANTITIES GREATER THAN 10^6 LBS.
PER YEAR AND WHICH SHOW A SIGNIFICANT HAZARD

Chlorosulfonic Acid	Acetaldehyde	Methyl Methacrylate	Turpentine
Phosphorus Pentasulfide	Butenes	Aniline	Isopropyl Acetone
Acetone Cyanohydrin	Phosphorus	Butyl Alcohol	Ethyl Acetate
Isoprene	Carbon Tetrachloride	Potassium Hydroxide	Nonene
DDT	Napthalene	Trichloroethane	Chlorobenzene
Cyclic Rodenticides	Perchloroethylene	Ethanolamines	Chloroform
Cyclic Insecticides	N-Propyl Alcohol	Aluminum Fluoride	Barium Carbonate
Sulfur	Trichloroethylene	Perchloric Acid	Tetramethyl Lead
Calcium Fluoride	Tetraethyl Lead	Maleic Anhydride	Dichlorobenzene
Calcium Carbide	Methyl Ethyl Ketone	Sodium	Dinitro Aniline
	Ammonium Perchlorate		

remainder of the study. Further details on the derivation of the list are presented in Section 4.0. Data were collected on degree of hazard and on infrared spectra for these materials. Infrared spectra show that most (over 90%), but not all, of these materials should be identifiable by an IR absorption instrument system.

1.3 Promising Instrument Approaches

Sections 5.0, 6.0, and 7.0 of this report are devoted to a review of specific instrument types, with an emphasis on evaluating their applicability to hazardous material detection. Table 1.2 summarizes the principal instrument types evaluated, with brief comments on their status (a few instrument types which show little promise, or which serve functions other than detection are discussed in the body of the report, but omitted here). Those instruments with significant promise for future development are discussed briefly in the paragraphs that follow.

The development of a remote instrument to identify a hazardous material out of a large number of possibilities poses formidable problems, discussed at length in Section 5.0. To date, no known instrument which is capable of performing this function has reached the hardware stage. Designing and building such an instrument at the laboratory level would be a difficult task. Making such an instrument to be rugged, portable, and easy to operate is far more difficult yet.

The instrument type which holds the most promise for eventual application to multi-hazardous material detection would be a development of the U.S. Army XM21. This instrument is, itself, in the developmental stage, but it is designed for operation by a soldier in the field, and is thus to be rugged and portable. The instrument is intended for use with a relatively small group of organophosphate materials. Thus, the major development for hazardous material application beyond verifying that the Army model can perform as planned in field tests, is the design of a microcomputer-based discrimination subsystem. Further details on the present system and requirements for its

Table 1.2 - Major Instrument Types Evaluated

Instrument Type	Reference Section	Remote/Non-Remote	Developmental Status	Comments
Passive IR Absorption	5.2.2.1, 5.4	remote	Developmental Stage	Potential for portable instrument, multi-material detection. Signal/Noise/Background problems can be significant. Development of U.S. Army XM21 system is most promising remote approach.
Active, Double-Ended Direct Absorption	5.2.1.1, 5.4	remote	Developmental/operational stage	A mobile van operational version exists. Possible adaptation of XM21 to this mode.
Laser Raman Scattering	5.2.1.3	remote	Developmental Stage	Multi-material capability; potential eye hazards; high power required. Large mobile versions have been built.
Laser Differential Absorption & Scattering	5.2.1.2	remote	Lab-type; operational	Many systems designed for single materials; multi-material systems at present very complex or limited in number of materials.
Correlation Spectroscopy	5.2.2.3, 6.2.1.1	remote or non-remote	Commercially available	Suited only for single material or small number of materials.
Non-Dispersive or Discrete Frequency Absorption	6.2.1.1	non-remote	Commercially available	Suited only for single material or small number of materials.
Dispersive Absorption	6.2.1.2	non-remote	Commercially available, but without discrimination subsystem	Potential for portable instrument, multi-material detection. Production models would require mainly development of discrimination subsystem.
Mass Spectroscopy or GC/MS combination	6.2.2, 6.2.4	non-remote	Developmental stage for portable version	Potential for portable instrument, multi-material detection.
Gas Chromatography	6.2.3	non-remote	Commercially available	Suitable for complex material separation, but not primary detection & identification.
Detector Tube Kits	6.2.5.1.1	non-remote	Commercially available	Available for many materials, but cumbersome where material identity is not known. Useful for monitoring known materials.
Chemical Kits	6.2.5.1.2, 6.2.5.1.3	non-remote	Developmental/operational stage	Useful for water analysis, analysis of solids or non-volatile liquids, or detecting general presence or absence of <u>some</u> hazardous material.
Combustible Gas Detectors	6.2.5.2.1	non-remote	Commercially available	Useful to monitor explosive or flammable concentrations, but not to identify materials.
IR Hot Spot Detectors	7.4	remote	Commercially available	Useful in various phases of firefighting.

application to hazardous material detection are given in Section 5.4.

If a detection instrument is not to operate remotely, but is able to perform some analysis on a sample of the material in question, the task is simplified somewhat. A large number of commercial and developmental instrument types are reviewed in Section 6.0. The instrument which shows the greatest potential for near-term development for hazardous material detection is a Dispersive Infrared Analyzer. Such instruments are commercially available in portable versions. As with a remote instrument, the aspect which needs development is a discrimination subsystem which would enable the instrument to compare a measured spectrum with data stored on many hazardous materials for quick identification.

The other non-remote instrument type which shows some promise for general hazardous material identification is a portable Gas Chromatograph/Mass Spectrometer. This instrument, described in Sections 6.2.2 and 6.2.4, is to be assembled from miniaturized components developed for spacecraft use. The present program is in its early stages; however, plans call for an emphasis specifically on hazardous materials, and include development of a computer data bank tie-in system.

With the emphasis on instrumentation, the potential of the human senses as an aid to material identification should not be overlooked. Training programs to help emergency personnel learn to recognize sensible manifestations of hazardous materials can be valuable and should be implemented.

Other techniques with more limited application or potential for development are commented on briefly in Table 1.2 and discussed at greater length in Sections 5.0, 6.0, and 7.0.

1.4 Recommended Actions

Detailed recommendations are contained throughout the report, and are summarized in Section 8.0. The following types of actions can be identified as important for FEMA in its role as responsible agency for hazardous material mitigation research:

- Support of programs to develop hazardous material detection instrumentation.

Depending on research funds available, the passive remote IR detection system and one or more of the possible non-remote systems should be developed. The development of a non-remote instrument based on existing Dispersive IR Analyzers should be achievable within a year. Development time of a remote instrument is harder to predict, but because of the attractiveness of such a system, it should be supported with a high priority.

- Continuing monitoring of instrument development in areas related to hazardous material detection.

Because of the rapid progress in instrumentation technology, the continuing close monitoring of developments in related fields is important so that timely application to hazardous material detection can be made. Some specific areas (some of them overlapping) are IR detection technology, interferometer design, detector and cooling system technology, laser system applications, pollution monitoring programs, military chemical agent-detection programs, NASA-sponsored space exploration instrumentation development, and microcomputer data analysis applications.

Means of maintaining this monitoring function are close liaison with related programs and agencies, review of current literature, and attendance at key conferences such as the Bi-Annual National Conference on Control of Hazardous Material Spills and the Annual Symposium of the Society of Photo-Optical Instrumentation Engineers.

- Development of a definitive list of hazardous materials for FEMA missions.

Various agencies, e.g., EPA, the Department of Transportation, and the Coast Guard, have developed lists of

materials defined as hazardous, according to criteria pertinent to their interests. Within the scope of time and funds available for this study, a list of materials posing significant hazards, and likely to be encountered in an accident, was compiled. However, a more definitive list based on more extensive statistical data can and should be developed.

- Support of programs to develop instrumentation for roles in hazardous material emergency operations other than identification.

Though the focus of this study was on instruments to identify an unknown material, instruments for other uses have been evaluated and commented on. Even if funds are limited, instrumentation needs for the entire range of response activities should be considered. Some specific types touched on in this report are alarms, personnel dosimeters or monitors, instruments for investigation of causes of accidents, and systems for obtaining material samples remotely or semi-remotely.

2.0 INTRODUCTION

2.1 Background

Almost daily one can pick up a newspaper and read an account of a hazardous material accident somewhere in the U.S. With the increased sophistication in the manufacture of complex chemical compounds, with the increased use of synthetic materials for many consumer products, and with the growing need for chemical reagents and processing materials for items ranging from textiles to semiconductor diodes, the transportation and handling of hazardous materials is a growing problem. A few statistics: the number of hazardous material transportation incidents reported by the U.S. Department of Transportation for 1977 was 15,954, a 34% increase over the number reported for 1976 (1, p. 21); it has been estimated that the number of hazardous material spills, excluding oil, entering the nation's navigable waters is 3,000 annually (2); and the number of railroad derailment accidents (not limited to hazardous materials) increased from 4960 in 1967 to 7981 in 1977 (3). Not only are primary hazardous materials a problem, but hazardous wastes are a growing menace. An article in the Philadelphia Inquirer estimates that Pennsylvania industry each year generates 10 times the amount of hazardous waste of which the state can safely dispose (4).

The number of hazardous material accidents and incidents calls for efforts in many areas: prevention, strategy and planning to meet emergencies, mitigation and control efforts during the response to an accident, and cleanup and investigation after an accident. This particular study is directed toward one phase of mitigation and control, with emphasis on the early time period of accident: that of detecting the presence of, and identifying, various hazardous materials.

On June 25 and 26, 1979, a Hazardous Materials Conference was held at the National Fire Academy in Emmitsburg, MD, sponsored by the Defense Civil Preparedness Agency (DCPA), which was soon to be incorporated into the newly organized Federal

Emergency Management Agency (FEMA). At this conference, members of government agencies concerned directly or indirectly with hazardous materials met to help establish priorities and plan for FEMA-sponsored research activities. A significant concern expressed at this meeting was the need for instrumentation to rapidly and accurately identify unknown hazardous materials in accident situations. Material identification was seen as the key to virtually all response activities; contingency plans and information sources such as CHEMTREC would be of little use until a material was identified.

At this conference, the groundwork for the present study was laid, and its direction was defined. The following sections will identify in more detail the objectives of this study, the methods used, and the scope of the work.

2.2 Objectives

The objectives outlined in the Work Plan for this study are as follows:

1. Compilation of hazardous materials most likely to be encountered in FEMA emergency missions.
2. Determination of exploitable chemical and/or physical characteristics of those materials.
3. Evaluation of the state of pertinent detection technology.
4. Establishment of operational and performance requirements for any detection technique deemed practical.

The first of these objectives is covered in Section 4.0 of this report, where a selected list of hazardous materials is presented, and the methods used for their selection are discussed.

Section 4.0 also presents pertinent chemical/physical data on the materials, principally in the form of information from several different ranking systems on degree of hazard for the materials and in data on infrared absorption spectra. In addition, pertinent physical or chemical properties as they relate

to one or other specific detection technique are discussed in the sections on those techniques (Sections 5.0, 6.0, and 7.0).

The third objective, evaluation of the state of pertinent detection technology, forms the burden of Sections 5.0, 6.0, and 7.0. There the many possible techniques for application to hazardous material detection are reviewed, with the degree of detail dependent on the likelihood of a given technique seeing application or development specifically for hazardous materials use.

The final objective is also covered in Sections 5.0, 6.0, and 7.0 with summary comments in Section 8.0, Conclusions and Recommendations. Requirements for future development are discussed most extensively for the passive, remote IR system and the dispersive, non-remote IR system which are seen as the most promising techniques. For other techniques, briefer comments on development needs are included in the sections which discuss those instruments.

2.3 Methods

The major work of this study consisted of the collection and evaluation of large amounts of information on hazardous materials, their properties, and on details of various instrument techniques.

For deriving the list of hazardous materials and compiling data on them, a variety of handbooks, regulations, published data collections, and journal articles were consulted. These are referenced in detail in Section 4.0.

The information on specific instrumentation techniques was obtained through personal discussions with researchers in the field, either in visits to their laboratories, or in telephone conversations. Extensive use was also made of product data sheets where instruments which have reached a production status were being evaluated. Finally, many published research reports or journal articles from the open literature were consulted. Wherever possible in the discussion of a particular instrument technique, specific references to the sources of information are given.

In Sections 5.0, 6.0, 7.0 and Appendix B, calculations and derivations of equations for quantities pertinent to the evaluation of some of the key techniques are presented.

Finally, as an aid to evaluating the experiences and needs of emergency personnel in the field, a survey of a group of emergency workers was taken. Some of the results of this survey are discussed in Section 3.0, and the details are presented in Appendix A.

2.4 Scope

A discussion of the scope of this study includes a consideration of the types of hazards included, the scope of information factored into the compilation of hazardous materials, the emphasis given to the evaluation of instruments, the extent of instrument techniques surveyed, and the amount of detail presented on various instrument types.

The emergency situations which this study addresses are those incidents, either in industry or in transportation, or caused by larger natural or wartime disasters, that involve potential hazards to the personnel responsible for corrective action as well as to the general public within the vicinity of the incident. The types of potential hazards include toxic, fire, explosion, and radiation (nuclear) hazards. Nuclear radiation hazards are specifically excluded from this study since many radiation detection devices have been developed and are in use. Thus, the materials considered hazardous for this study are principally those which are toxic, inflammable, or explosive.

As noted in Section 4.0, within the scope of time and funds available for this study, an extensive compilation of statistics on amounts of hazardous materials transported and on actual accidents involving specific materials was not possible. The compilation of hazardous materials made use of data on amounts of materials produced and previously conducted analyses or previously published handbooks. The length of the list, 115 materials, was intended to be suitable for an

instrument which would have a practical limit to the number of materials it could identify, either because of limitations in the detection mechanism or in the data storage/discrimination subsystem. A more detailed and extensive compilation and ranking of hazardous materials would seem to be of value to FEMA for its overall mission of mitigation and control of hazardous material accidents.

Of the possible instrument types and applications, the emphasis in this study was placed on those which would be portable, easy to use, and suitable for the first emergency group to arrive at the scene of an accident. The ideal instrument would be a small black box with few controls, usable by an inexperienced person, which could be pointed at a material or vapor cloud, and which would immediately identify the material and tell the concentration. No such instrument exists, nor possibly ever will exist, but the postulation of such an ideal instrument points to the emphasis of this study. The desirability of remote detection has led to an emphasis on remote instruments over those for which a sample of the material must be taken. Because of the predominance of production-level direct-sampling instruments over remote instruments, however, the consideration of direct-sampling instruments has led to a sizable section, Section 6.0, on that class of instruments. Emphasis was also placed on instruments which could determine the identity of a large number of possible materials, and hence be versatile in many accident situations. Occasional comments, especially in Section 6.0, are made on the possible application of an instrument technique beyond hazardous material detection/identification.

An attempt was made to include coverage of as many instrument types as possible in the evaluation of current technology. The coverage included instruments designed specifically for hazardous material use as well as instruments which could have some applicability to hazardous material detection, but which were designed primarily for these fields: industrial monitoring, air and water pollution control, military chemical warfare agent

detection, atmospheric studies (whether for pollution or "normal" constituents), and space exploration. Where many commercially-produced models of a certain instrument type exist, coverage is not intended to be exhaustive but, rather, information on representative models is cited. Further details related to the scope of coverage in this study are given in Section 3.0.

Because of the number of instrument types evaluated, an attempt was made to suit the detail presented to the relative importance of the instrument, and to keep the sections on instruments of limited applicability relatively brief. This report was planned, however, to serve as a useful reference for readers desiring to pursue information on a given instrument type in greater detail. As mentioned previously, references are given wherever possible to sources of information. References on production-level instruments include names and addresses of companies, which can be consulted for more information. In addition, a number of the references are review-type articles or reports, and are themselves sources of further extensive references on their particular topics. Thus, this report should be a useful starting point for anyone wishing to pursue information on a given instrument type in more detail.

3.0 NEEDS IN HAZARDOUS MATERIAL DETECTION AND IDENTIFICATION

Before entering into a discussion of various instrumentation types and techniques, it would be helpful to consider presently used methods of detecting and identifying hazardous materials and, from this information, to define instrumentation needs from the point of view of the emergency worker. This section will include a brief analysis of various accident scenarios, and a discussion of data from a survey of the experiences and needs of a group of emergency workers.

3.1 Present Methods of Identifying Materials

The National Fire Protection Association annually sponsors a series of seminars entitled "Handling Hazardous Materials Transportation Emergencies." The seminars, which are for the training of emergency personnel from a variety of organizations, reflect current widely used practices to plan for and handle hazardous material emergencies. The principal methods discussed in Unit Three, "Recognizing and Identifying Hazardous Materials in Transit," and Unit Four, "Obtaining Technical Assistance in Hazardous Materials Incidents," are the following (5):

- Reading labels and placards
- Identifying contents by size, shape, and type of container
- Reading package or container markings
- Obtaining and reading shipping papers
- Contacting transportation personnel
- Contacting CHEMTREC
- Using various emergency action guides, cards, or manuals

NOTE: Further information on labels and placards is given in Section 4.0.

As can be seen, all of the methods listed above are indirect; that is, none involves using an instrument to directly sample or measure a material. Moreover, several of the methods give information only on classes of hazardous material. For example, the labels and placards required by law may identify that a

material is flammable or corrosive, but they do not identify the chemical itself. Container shapes and physical characteristics also give only general indications, for example, that a material is a compressed gas. Contacting CHEMTREC can be useful to determine emergency procedures if the identity of the material is known; but if it is unknown, some information must be provided, for example, a tank car serial number. Tracking down material identity by tracing a tank car or truck to its originator can be time-consuming.

For positive material identification by indirect means, the only reasonably quick and sure methods are reading the name of a material on a container if it is there, or obtaining and reading shipping papers. There are many circumstances which can render either of these methods impossible to apply: containers are not labeled by contents; the person with shipping papers is injured or unavailable; shipping papers are deliberately falsified; labels or shipping papers are obscured because of damage by impact or because of smoke, or are burned beyond recognition; or intense heat or poison fumes prevent close enough approach to read labels or obtain shipping papers. In the survey of emergency workers discussed in detail in Appendix A, responses indicate that in only 67% of incidents were placards visible (placards identify only the class of material), and that in only 48% of incidents were shipping papers available. Thus, the experience of workers shows that many accidents occur where the material is not easily identifiable by indirect means.

Are any instruments used at all to help identify materials? The survey results presented in Appendix A show that 57% of the people surveyed used some form of instrument. However, 43% of those surveyed relied solely on the indirect means of attempting to read placards and shipping papers, calling CHEMTREC, etc. Moreover, of the instruments used (see Appendix A, p. 212) most, for example, explosimeters, are only applicable to limited classes of materials. The instrument now in use which has the most widespread applicability is the MSA Universal

Tester Kit and tubes (to be described in more detail in Section 6.2.5.1.1). However, even with this Universal Tester, as one emergency worker stated, "Various glass tubes must be inserted into the instrument. As a result, you must have some idea of what gas is present; otherwise, it would be an impossible job to go through each category."

From the point of view, then, of the methods now used in the field to identify materials, there is a definite need for some easy-to-use instrument which would allow positive identification of a material in those instances where indirect means are not sufficient. One can think of instrumentation needs from another point of view: that of considering the various events that might happen in a hazardous material accident, and determining what types of instrumentation might be useful to cope with these different stages of the accident. This point of view will be explored in the next section.

3.2 Hazardous Material Accident Scenarios

There are many different types of hazardous materials, and there are many types of accidents that occur. Most accidents happen while materials are being transported or handled in some way (although some recent accidents at deteriorating storage tanks indicate that this may not always be the case). Accidents can happen to any of the vehicles by which materials are transported: trucks, trains, ships, and airplanes; they can happen in and around pipelines; and they can happen while material is being transferred to a storage container.

Considering an accident from the most general perspective, whether it be a transportation or handling accident, one can examine the alternatives of what conditions might be present and how an emergency worker might respond to those conditions. Figure 3.1 shows in schematic form the major alternatives as they relate to actions that might require instrumentation.

The first major division of types of accidents is those in which there is a fire or explosion, and those in which there is none. The survey data in Appendix A shows that, from the

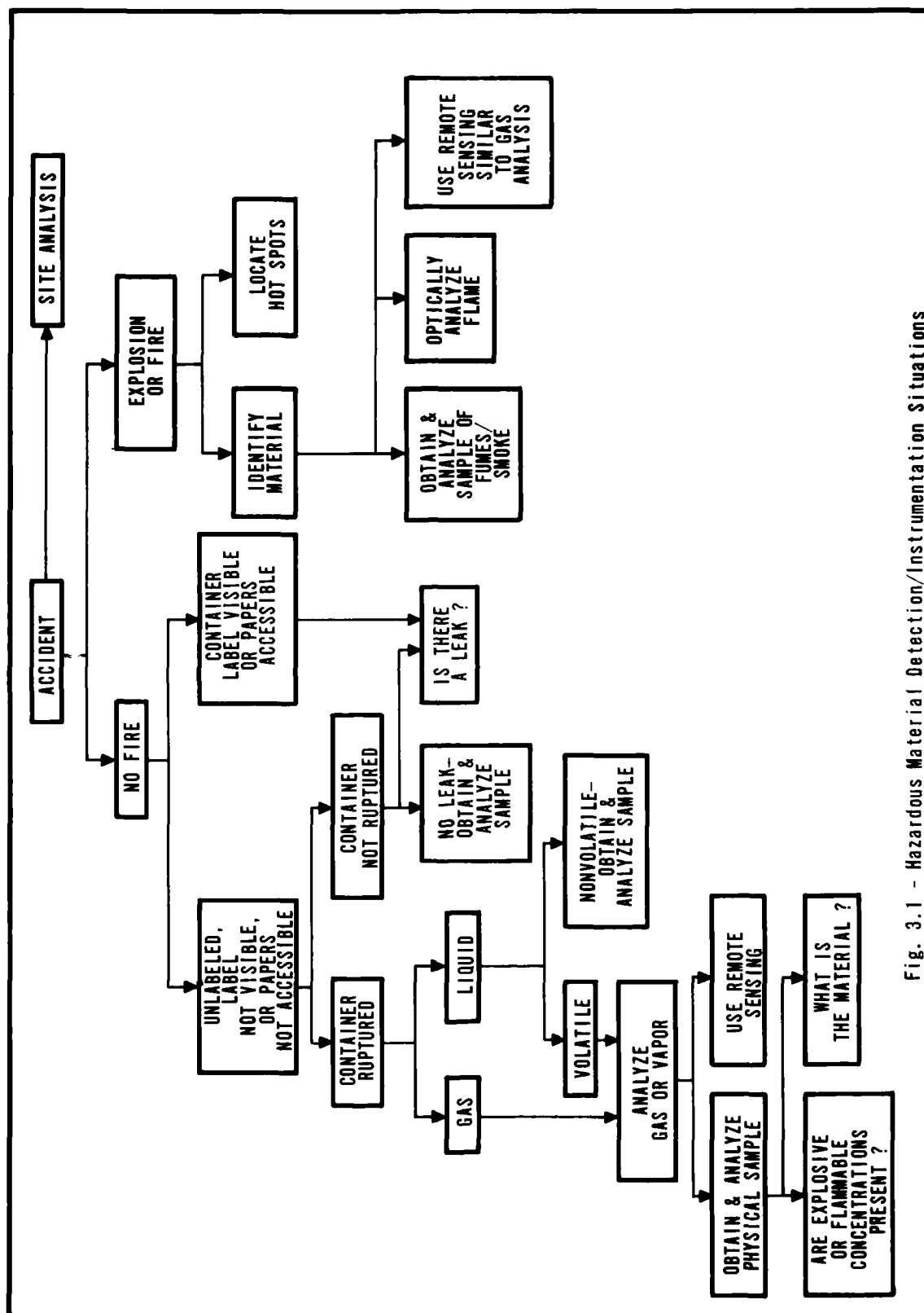


Fig. 3.1 - Hazardous Material Detection/Instrumentation Situations

experience of the workers questioned, approximately 28% of the hazardous material accidents which they had witnessed were accompanied by fire or explosion, whereas 72% had no fire or explosion.

In the case of no fire or explosion, the material may be identifiable by papers or labels. If it is not identifiable, the problem of determining what materials are present depends on the condition of the container. If the container is relatively intact, the possibility of obtaining a sample and analyzing it in some way presents itself. At the same time, checks to see that there were no small leaks in the container would be of value. If the container is obviously ruptured and venting a gas or leaking a liquid, with the possibility of poisonous vapors or an imminent explosion, the problem of identification becomes more difficult. With the help of protective clothing, a worker could still obtain a physical sample for analysis. However, the use of a remote sensing device, if one were available, would be much safer. Possibilities for remote sensing instrumentation are considered in Section 5 of this report, and various techniques for analyzing samples are discussed in Section 6.0. Methods for analyzing leaks were not given extensive treatment in this study, but are mentioned briefly at the end of Section 6.0.

If an explosion or fire occurs, the problem of identifying the material is also difficult. There may still be instances where labels are visible, but the likelihood of their being charred or obscured by smoke is high. Shipping papers may also be accessible, but often only at great risk to the person trying to obtain them. As with the non-fire case, the alternatives of working remotely or of obtaining samples (unburned materials or fume/smoke samples) are present. Again, the safer or more convenient method would be remote sensing, if this were possible. Finally, in the case of fire, particularly in the later phases of fire fighting, the possibility of an instrument to detect hot spots could be considered. Such an instrument would be of value when working in dense smoke where flames or embers were

not visible to the eye, or in checking an area for smoldering spots after the main blaze was extinguished. Remote heat detectors will be discussed in Section 7.0.

A class of instruments that is not considered in detail in this report is those related to site analysis. One can think of needs such as determining wind direction, velocity, and other weather conditions; terrain conditions as they might affect water runoff and eventual pollution of water supplies; and the existence of possible complicating conditions such as the presence of electrical wires or sources of ignition. Instruments or techniques for site analysis are assumed to be relatively well-developed, and are not discussed further.

Another point of view from which to consider a hazardous material accident is the different time frames in which responses may occur. Table 3.1 divides responses into immediate, intermediate, and long-term. While the dividing lines between these time frames are not precise, conceptually it can be helpful to think of responses according to these divisions. The immediate time frame applies to the first people at the scene of an accident and their efforts to assess its severity, plan strategy, minimize casualties, and prevent serious complications from arising. The intermediate response time may cover a period anywhere from hours to several days, and is the time during which continuing mitigation and control efforts occur. Finally, long-term response is related mainly to efforts at cleaning up an area, restoring it to its original condition, or at least a safe condition, and possibly conducting investigations into the causes of the accident.

The emphasis of this study, as noted in the Introduction, will be on the immediate response time frame. Less emphasis will be given to the intermediate time frame, and even less to long-term response, although instruments or techniques as they apply to these time regimes will be pointed out.

Table 3.1 - Instrumentation Needs
in Terms of Response Time

Immediate Response - First People on Scene

- Identify Class of Material or Generic Properties (Toxic, Explosive, Etc.)
- Determine Severity of Hazard
- Take Immediate Action for Fire Control, Evacuation, Etc.
- Avoid Complication by Wrong Response Action
- Plan Strategy

Instrument Requirements: Lightweight, Portable, Simple to Operate, Inexpensive

Intermediate Response

- Identify Materials More Precisely
- Guide Efforts at Mitigation/Control
- Plan Further Evacuation or Re-occupancy of an Area
- Plan Cleanup

Instrument Requirements: Mobile (E.g., Van, Copter), Relatively Inexpensive

Long Term Response

- Further Identify Problem Materials
- Detect Allowable Levels for Cleanup Operations
- Investigate Causes of Accident

Instrument Requirements: Relatively Mobile, Highly Sensitive

4.0 A LIST AND CATEGORIZATION OF MATERIALS

4.1 Introduction

The answer to the question, "What is a hazardous material?" will vary, depending on the concerns of the agency or group addressed. A number of lists have been developed by government and private agencies classifying materials as hazardous according to differing criteria. Both the specific materials and the total number of materials included vary significantly from list to list.

It is the purpose of this part of the study to derive a list of materials which will meet the following criteria:

- a. The materials included should be those which can be considered hazardous in terms of FEMA emergency missions and requirements.
- b. The list should be "manageable" in length, in view of the likely limitation in the number of materials detectable by any field instrument.
- c. The list should rank materials, at least to some extent, according to degree of hazard.

These criteria will be discussed further in Section 4.2.2 where the final list is presented.

An additional purpose of this part of the study is the compilation of relevant data on the materials in the list. For this study, the data includes information on the degrees of hazard for all of the materials, and, since an IR detection system is the most likely candidate for future development, information on IR spectral signatures of the materials is also included. An extensive compilation of what would be considered standard handbook data on these materials (e.g., density, boiling point) was not attempted.

4.2 Selected List of Hazardous Materials

4.2.1 Sources of Information

The resources drawn upon for this portion of the study consisted of lists of hazardous materials prepared by various

agencies, information on quantities of materials produced, handbook data on hazardous materials, and information from other studies which ranked materials by degree of hazard. Further details on the key sources will be given in the following paragraphs. A number of sources of historical data exist on quantities of materials transported (6,7,8)* and on actual accident statistics (1,6,7,8,9,10). However, this information was not factored into the selection of materials for the present list because (a) the information was too general, i.e., on classes rather than on specific materials, and/or (b) the compilation and analysis of the data would extend beyond the scope of the present contract. A more definitive assessment of hazardous materials as they relate to FEMA missions should be conducted, and such a study should take into account as much statistical and historical information of this type as possible.

4.2.1.1 Regulations

Two key lists define materials as hazardous for purposes of regulation. These lists appear in the Code of Federal Regulations Title 40 (CFR 40) - Protection of the Environment (11) and Code of Federal Regulations Title 49 (CFR 49) - Transportation (12).

CFR 40 lists "substances" (elements and compounds) under the jurisdiction of the Environmental Protection Agency (EPA) that are considered to be hazardous in terms of water pollution. The list, which is updated periodically, contained 271 substances as of an amendment dated June 26, 1978. Part 118 of CFR 40 provides a coarse ranking of degree of hazard in terms of a minimum amount of the substance which, if discharged,

*According to a private conversation with Joseph Malevanko, Materials Transportation Bureau, Department of Transportation, on 6 November 1979, no comprehensive set of statistics exists on amounts of specific materials transported by various means. References 6-8, however, are examples of reports which present information on quantities transported for various groups of materials or modes of transportation.

would be harmful to the aquatic environment. Each substance is assigned to a category according to the following letter scheme:

<u>Category</u>	<u>Minimum Harmful Quantity</u>	
	<u>(pounds)</u>	<u>(kilograms)</u>
X	1	0.454
A	10	4.54
B	100	45.4
C	1000	454.0
D	5000	2270.0

This ranking system, however, does not necessarily relate to degree of hazard to emergency personnel. Many substances can be harmful to aquatic life in small amounts, but would pose no serious threat to the first people on the scene of an accident. Also, many of the substances in the EPA list are produced or shipped in small quantities, so that the likelihood of their being encountered in a serious accident is small.

CFR 49 lists approximately 1400 materials which are considered to pose a significant enough hazard in interstate transportation that the conditions of their shipment are to be regulated. The materials are not ranked according to degree of hazard (although some details of their marking, e.g., "Flammable Liquid" relate to type of hazard); nor is the list determined on the basis of any frequency of transport or quantity produced. More so than with the EPA list, there will be many materials with a relatively low probability of being encountered in an accident.

4.2.1.2 Other Sources

Numerous lists of hazardous materials exist other than those developed for regulation. Several of the more significant lists will be discussed here in order to illustrate the differences in number of materials and criteria according to which they are included.

The U.S. Department of Transportation has published an Emergency Action Guide for Selected Hazardous Materials (13). This booklet lists, alphabetically, 44 materials "shipped in bulk that are gaseous or highly-volatile liquids with poisonous or extremely flammable properties." The booklet was intended to help emergency personnel during the first 30 minutes of an accident involving a material that could pose serious hazards. This list does not rank materials, but by its selectivity it is useful in identifying materials with a high degree of hazard.

The National Fire Protection Association (NFPA) publishes a number of handbooks, two of which are pertinent to hazardous material evaluation: Hazardous Chemical Data and Fire Hazard Properties of Flammable Liquids, Gases, and Volatile Solids. (14) The first of these handbooks provides, for several hundred hazardous chemicals, a qualitative rating of degree of hazard in three areas: health, flammability, and reactivity. Each of these three categories of hazard is assigned a number ranging from 0 (no hazard) to 4 (severe hazard), and the numbers are displayed in a diamond scheme as shown below.

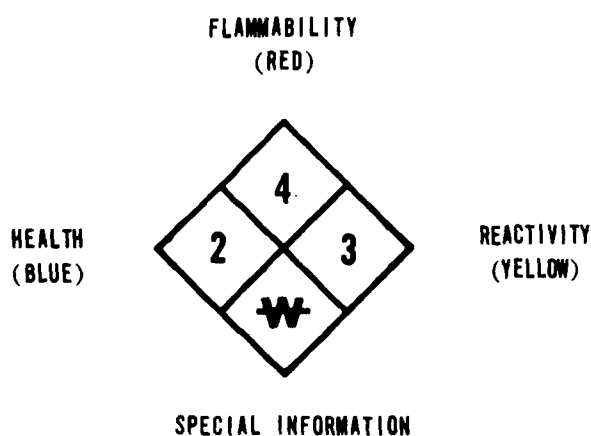


Fig. 4.1 - NFPA Hazard Rating Scheme

The colors listed refer to the colors of numerals or the background if this scheme is used as a label on containers or vehicles. The fourth box, "Special Information" may be left blank, or may point out special precautions. In the example shown, the symbol means that no water should be used. This NFPA rating scheme is one for which information will be presented in our selected list of hazardous materials.

The most compendious listing of hazardous materials is Sax's Dangerous Properties of Industrial Materials (15). As the title indicates, the basis for selection and data presentation in this compilation is industrial safety. The information, however, is useful for general assessments of material hazards. Sax's book lists, alphabetically, thousands of materials ranging from the most commonplace, for example, "rags" (oily or wet), to the most exotic chemicals. The manner in which information is presented on each material tends, unfortunately, to be somewhat uneven. For many materials, hazard ratings are given according to a four-digit numerical scheme covering 0 (no hazard) to 3 (high hazard); for other materials, a verbal, descriptive analysis is given. Some of the information on toxicity, for example lethal dose levels for ingestion, would have little relevance for accident emergency response; however, information on inhalation would be very pertinent.

The U.S. Coast Guard maintains the Chemical Hazards Response Information System (CHRIS), a major element of which is the CHRIS Manual of data on approximately 900 hazardous materials (16). These materials, as with the EPA list, are chosen with reference to water, but with the emphasis on bulk transport (including hazards to personnel as well as to the environment). In a preliminary step to setting up the CHRIS data system, the Coast Guard sponsored a study by the National Research Council of the National Academy of Sciences (NAS). Their report (17) includes a discussion of a hazard-rating system applied to several hundred industrial chemicals transported in bulk on U.S. waterways. Briefly, the system provides a 5-level numerical rating somewhat similar to the NFPA system,

but covering the areas of fire, health, water pollution, and reactivity, with several subdivisions under each category. These numerical rankings are included in our selected list of materials for those chemicals covered by the NAS report.

As a step to setting up the list of materials regulated by CFR 40, discussed previously, the EPA commissioned a study by Battelle Northwest to classify and rank hazardous materials (6). This study is concerned with hazards according to the same criteria as CFR 40, namely, water pollution. The study includes ranking both of quantities of materials produced, according to U.S. Department of Commerce data, and of severity of hazard. This second ranking, it is emphasized again, includes hazards as they relate to water pollution; therefore, the numerical ranking was not factored into our list. However, the information on quantities produced, though somewhat outdated*, was used to derive a part of our list. The EPA has also more recently sponsored the development of an extensive computer-based data bank called OHM-TADS (Oil and Hazardous Materials Technical Assistance Data System) (18). This system, though it provides extensive data on approximately 1,000 materials, does not rank materials, and was not used in the derivation of our list.

One of the purposes of the preceding discussion has been to indicate the variety of sources and variety of ranking systems that exist. Drawing on this information, we have attempted to derive a selected list of materials as they pertain to FEMA needs and to this study. Some additional topics related to the selection of materials are discussed in the following section.

4.2.2 Rationale for Selection

The materials selected in this program, and their hazardous properties, are listed in Table 4.1. This table includes

*G.W. Dawson, one of the authors of the Battelle Report, indicated in a private conversation that, to his knowledge, no significant updating of a study of this type has been conducted since 1970.

the material names (along with common synonyms, where appropriate); an identification of the normal state of the material, whether gas, liquid, or solid; information on hazardous properties (to be discussed in Section 4.3); and special comments on certain materials.

The 115 materials in Table 4.1 are divided into three groups according to the following criteria:

GROUP I: Chemicals chosen from the list published by Chemical and Engineering News of the 50 chemicals produced in greatest quantities in the U.S. (19).

This group represents materials produced in very large quantities, which would, therefore, have a relatively high probability of being encountered in an accident, and which show a significant hazard level. "Significant" in this context means being ranked at a level of 3 or higher in at least one category of at least one of these rating schemes: NFPA (14), U.S. Coast Guard (17), and Sax (15). An exception would be a material which showed a high chronic toxicity rating (for repeated exposure) in Sax, but no other hazard. Such a material would not be considered as a significant hazard for the single encounter of emergency personnel.

The materials in this group are listed in decreasing order of quantities produced according to the 1979 listing.

Because Chemical and Engineering News does not include "petrochemical feedstocks" in its list, a subgroup, Group IB, of very flammable products known to be shipped in large quantities was added. These materials were selected on the basis of having an NFPA flammability rating of 2 or higher.

GROUP II: Those materials not included in Group I which are listed in the DOT guide Selected Hazardous Materials (13).

This group represents materials produced in smaller quantities than the materials in Group I, but which are shipped in bulk and which are highly hazardous. The criteria for inclusion stated in the DOT guide are bulk materials that are "gaseous or highly volatile liquids with poisonous or extremely flammable properties." The materials in this group are simply listed alphabetically.

GROUP III: Materials not included in Groups I or II, which are produced in large quantities according to the 1970 Battelle Study (6), and which show a significant hazard level.

This group represents materials with generally less severe hazards than those in Group II, but which are produced in very large quantities, making the probability of encounter relatively high. The same criterion for determining "significant" hazard as was used for Group I has been applied. An arbitrary cutoff point for quantities produced was set at 10^6 pounds per year according to the 1970 figures. The materials in this group are listed in decreasing order of quantity produced according to the Battelle ranking.

It should be emphasized that the list presented here is not meant for design purposes, but rather is intended as illustrative of the variety of hazardous materials to be encountered in emergency missions. This list was compiled without regard to the ease of detection of any given material (for example, several solids are not amenable to many detection methods). Also, as mentioned earlier, the derivation of this list did not include statistics on amounts transported or on previous actual accidents. The number of materials in the list was determined by a somewhat arbitrary cutoff point; the list could

be continued virtually indefinitely if an instrument which could detect more than a hundred or so materials could be developed.

Any list which is derived for the purpose of deciding what material data is to be factored into the design of an instrument should be based on studies which reflect the most up-to-date and realistic data. Such studies should include projections of the probabilities of accidents based on mode of transportation and mode of containment, and these projections should be backed up where possible by historical data. In the practical situation, local variations in the probability of encountering certain materials might be taken into account. Thus, in an area where certain materials are produced and frequently transported, a detector data system might be programmed to include these materials, even though they did not rank high on a national level.

One final comment: the materials listed include both pure chemicals and mixtures, or groups of materials. Thus, "gasoline" and "kerosene," both mixtures, are included because they are frequently encountered. Some of their principal components, pentane, hexane, etc., are also included because they are shipped in their pure state. Infrared (or other) spectral signatures are relatively easy to specify for pure compounds. However, the problem of identifying mixtures through spectral data is a difficult one which should be addressed in any detailed study of adapting an instrument to actual emergency encounters.

4.3 Hazard Data

Information on the relative hazards of materials in our list has been compiled, and is included in Table 4.1. As mentioned in Section 4.2.2, the numerical ranking according to one of several hazard rating schemes was used as a criterion for including materials in the list. However, whether or not the rating in a certain category was high, it has been included, where the information existed, for the sake of completeness.

Table 4.1 - Selected List of Hazardous Materials									
MATERIAL	STATE (SOLID, LIQUID, GAS)	NFPA RATING	COAST GUARD RATING				RATING BY SAX	EPA CATEGORY	COMMENTS
			FIRE	HEALTH	WATER	REACT			
GROUP 1A									
Sulfuric Acid (Oil of Vitriol; Oleum)	L		0	4	3	4	3	C	Oleum is Sul- furic acid & SO ₃
Oxygen	G/L		—				—	—	
Ammonia, Anhydrous	G		1	4	3	3	3	B	
Ethylene (Ethene)	G		4	1	1	2	2	—	
Chlorine	G		0	4	3	4	3	A	
Sodium Hydroxide (Lye, Caustic Soda)	S		—				3	C	May also be shipped in (water) solution
Phosphoric Acid	L/S		0	3	3	3	2	D	
Nitric Acid	L		0	4	3	4	3	C	
Ammonium Nitrate	S }		NO FIRE				1	—	
			FIRE						
Propylene	G		4	1	1	1	2	—	
Benzene	L		3	3	3	1	3	C	
Ethylene Dichloride (1,2 - Dichloroethane)	L		3	3	3	1	3	—	

Table 4.1 - Selected List of Hazardous Materials (Cont'd.)

Table 4.1 - Selected List of Hazardous Materials (Cont'd.)									
MATERIAL	STATE (SOLID, LIQUID, GAS)	NFPA RATING	COAST GUARD RATING				RATING BY SAX	EPA CATEGORY	COMMENTS
			FIRE	HEALTH	WATER	REACT.			
GROUP 1A (Cont'd.)									
Toluene	L		3	2	3	1	2	C	
Ethylbenzene	L		3	2	3	1	2	C	
Vinyl Chloride	G		4	2	0	2	3	—	
Styrene	L		3	2	3	3	2	C	
Formaldehyde	G		WATER SOLUTION 2 3 3 2 (Solution)				3	C	May be shipped in solution
		GAS							
Methanol (Methyl Alcohol)	L		3	2	1	3	3	—	
Xylene	L		3	2	3	1	2	C	
Hydrochloric Acid (Hydrogen Chloride)	G/L		0	3	2	3	3	D	
Ethylene Oxide	G		4	3	3	4	3	—	
Ethylene Glycol	L		1	1	2	2	3	—	
Ammonium Sulfate	S		NO FIRE				1	—	
			FIRE						

Table 4.1 - Selected List of Hazardous Materials (Cont'd.)

Table 4.1 - Selected List of Hazardous Materials (Cont'd.)									
MATERIAL	STATE (SOLID, LIQUID, GAS)	NFPA RATING	COAST GUARD RATING				RATING BY SAX	EPA CATEGORY	COMMENTS
			FIRE	HEALTH	WATER	REACT.			
GROUP 1A (Cont'd.)									
Butadiene	G		4	1	1	3	2	—	
Cumene	L		2	1	3	1	3	—	
Acetic Acid	L		2	3	2	2	3	C	
Phenol	S		1	3	3	2	3	C	
Cyclohexane	L		3	2	2	0	2	C	
Acetone	L		3	1	1	2	2	—	
Propylene Oxide	L		4	3	2	3	2	—	
Acrylonitrile	L		3	3	4	3	3	B	
Isopropyl Alcohol (Isopropanol)	L		3	2	2	2	2	—	
Vinyl Acetate	L/S		3	2	2	3	1	C	
Acetic Anhydride	L		2	3	2	3	3	C	
Ethanol (Ethyl Alcohol)	L		3	1	1	2	2	—	
GROUP 1B									
Gasoline	L		3	2	2	0	2	—	Various grades

Table 4.1 - Selected List of Hazardous Materials (Cont'd.)									
MATERIAL	STATE (SOLID, LIQUID, GAS)	NFPA RATING	COAST GUARD RATING				RATING BY SAX	EPA CATEGORY	COMMENTS
			FIRE	HEALTH	WATER	REACT.			
GROUP 1B (Cont'd.)									
Kerosene & Jet Fuels	L		3	1	3	0	2	—	e.g., JP-3, JP-4, JP-5
Fuel Oils	L		—				—	—	e.g., No.'s 2, 4, 5, 6
Ethane	G		—				2	—	
Propane (LPG)	G/L		4	0	0	0	2	—	
Butane (LPG)	G/L		4	0	0	0	2	—	
Isopentane	L		4	1	2	0	1	—	
Isobutane	G/L		—				1	—	
Pentane	L		4	1	2	0	1	—	
Hexane	L		3	1	1	0	1	—	
Heptane	L		3	1	2	0	2	—	
Octane	L		—				2	—	
Natural Gas (LNG)	G/L		4	0	0	0	2	—	Primarily Meth- ane (83-99%)
Acetylene	G		—				2	—	Often shipped dissolved in acetone

Table 4.1 - Selected List of Hazardous Materials (Cont'd.)									
MATERIAL	STATE (SOLID, LIQUID, GAS)	NFPA RATING	COAST GUARD RATING				RATING BY SAX	EPA CATEGORY	COMMENTS
			FIRE	HEALTH	WATER	REACT.			
<u>GROUP II</u>									
Acrolein	L		3	4	4	3	3	X	
Boron Trifluoride	G						3	—	
Bromine	L						3	—	
Carbon Disulfide	L		4	3	3	2	3	D	
Dimethyl Ether	G						2	—	
Dimethyl Sulfate	L						3	—	
Epichlorohydrin	L		3	4	3	3	3	—	
Ethyl Chloride	L		4	1	1	1	2	—	
Ethyleneimine	L		3	4	3	3	3	—	
Fluorine	G						3	—	
Hydrogen	G/L						1	—	
Hydrogen Cyanide (Hydrocyanic Acid)	G						3	A	
Hydrogen Fluoride (Hydrofluoric Acid)	G/L		0	4	4	3	3	D	

Table 4.1 - Selected List of Hazardous Materials (Cont'd)

MATERIAL	STATE (SOLID, LIQUID, GAS)	NFPA RATING	COAST GUARD RATING				RATING BY SAX	EPA CATEGORY	COMMENTS
			FIRE	HEALTH	WATER	REACT.			
Hydrogen Sulfide	G		---	---	---	---	3	---	
Methane	G/L		4	0	0	0	1	---	primary constituent of Natural Gas (83-99%)
Methylamines	G		---	---	---	---	3	C	Mono-, Di-, and Tri- are important varieties
Methyl Bromide	L		1	4	2	1	3	---	
Methyl Chloride (Chloromethane)	G		4	2	1	1	3	---	
Methyl Ethyl Ether (Ethyl Methyl Ether)	G/L		---	---	---	---	---	---	
Methyl Mercaptan	G/L		---	---	---	---	2	B	
Nitrogen Tetroxide	G		---	---	---	---	3	C	
Phosgene	G		---	---	---	---	3	D	
Phosphorus Trichloride	L		---	---	---	---	3	D	
Sulfur Dioxide	G		---	---	---	---	3	---	
Titanium Tetrachloride	L		---	---	---	---	3	---	
<u>GROUP III</u>									
Chlorosulfonic Acid	L	---	0	4	3	4	3	C	

Table 4.1 - Selected List of Hazardous Materials (Cont'd.)

MATERIAL	STATE (SOLID, LIQUID, GAS)	NFPA RATING	COAST GUARD RATING				RATING BY SAX	EPA CATEGORY	COMMENTS
			FIRE	HEALTH	WATER	REACT.			
Group III (Cont'd.)									
Phosphorus Pentasulfide	S		---				3	B	
Acetone Cyanohydrin	L		1	4	4	3	3	A	
Isoprene	L		4	1	1	3	2	C	
DDT	S	---	---				---	X	
Cyclic Rodenticides	S/L	(PARATHION)	---				3	X	Representative examples would be Aldrin, Parathion & Toxaphene
		(ALDRIN)	---				3	X	
		(ALDRIN) SOLUTIONS	---				3	X	
		(ALDRIN) DRY	---				3	X	
Cyclic Insecticides	S/L	(ENDRIN)	---				3	X	Representative examples would be Chlordane, Dieldrin, Endrin
		(ENDRIN) SOLUTIONS	---				3	X	
		(ENDRIN) DRY	---				3	X	
Sulfur	S/L		NO FIRE				---	---	
			3	1	1	4	---	---	
Calcium Fluoride	S	---	---				3	---	
Calcium Carbide	S		---				moderate	D	evolves acetylene






Table 4. Selected List of Hazardous Materials (Cont'd.)

MATERIAL	STATE (SOLID, LIQUID, GAS)	NFPA RATING	COAST GUARD RATING				RATING BY SAX	EPA CATEGORY	COMMENTS
			FIRE	HEALTH	WATER	REACT.			
Group III (Cont'd.)									
Acetaldehyde	L		4	3	3	2	3	C	
Butenes	G						---	---	
Phosphorus	S		3	4	4	4	3(white)	X	
Carbon Tetrachloride	L		0	2	2	1	3	---	
Napthalene	S		1	2	3	1	2	D	
Perchloroethylene	L	---	0	2	3	1	3	---	
N-Propyl Alcohol	L		3	2	2	2	2	---	
Trichloroethylene	L		1	2	2	1	3	---	
Tetraethyl Lead	L		1	4	3	3	3	B	
Methyl Ethyl Ketone	L		3	2	2	2	2	---	
Methyl Methacrylate	L		3	3	2	3	2	D	
Aniline	L		1	3	4	3	3	C	

Table 4.1 - Selected List of Hazardous Materials (Cont'd.)

MATERIAL	STATE (SOLID, LIQUID, GAS)	NFPA RATING	COAST GUARD RATING				RATING BY SAX	EPA CATEGORY	COMMENTS
			FIRE	HEALTH	WATER	REACT.			
Group III (Cont'd.)									
Butyl Alcohol	L		3	2	2	2	2	---	
Potassium Hydroxide (Lye)	S		---	---	---	---	3	C	
Trichloroethane	L		1	2	3	1	2	---	
Ethanolamine (2 - Aminoethanol)	L		1	2	2	3	2	---	
Aluminum Fluoride	S		---	---	---	---	3	---	
Perchloric Acid	L		---	---	---	---	3	---	
Maleic Anhydride	S		---	---	---	---	3	D	
Sodium	S		---	---	---	---	3	C	
Turpentine	L		3	1	3	1	3	---	
Isopropyl Acetone	L		---	---	---	---	3	---	
Ethyl Acetate	L		3	2	2	1	2	---	
Nonene (Nonylene)	L		3	1	2	1	---	---	
Chlorobenzene	L		3	2	3	1	2	B	
Chloroform (Trichloromethane)	L		1	2	2	1	3	D	

Table 4.1 - Selected List of Hazardous Materials (Cont'd.)

Table 4.1 - Selected List of Hazardous Materials (Cont'd.)									
MATERIAL	STATE (SOLID, LIQUID, GAS)	NFPA RATING	COAST GUARD RATING				RATING BY SAX	EPA CATEGORY	COMMENTS
			FIRE	HEALTH	WATER	REACT			
Table III (Cont'd.)									
Barium Carbonate	S	---	---				3	---	
Tetramethyl Lead	L		1	4	3	1	high	---	
Dichlorobenzene	L/S		1	2	3	1	3	---	
Dinitro Aniline	S		---				3	---	
Ammonium Perchlorate	S		NO FIRE				2	---	
									

A few additional comments should be made about the hazard data presented in Table 4.1:

- 1) The NFPA ratings are presented according to the scheme described in Section 4.2.1.2.
- 2) In the column headed "Coast Guard", numerical ratings are presented under four headings: Fire, Health, Water, and Reactivity. In the original Coast Guard Study (17), these categories were further subdivided; for example, "Health" was divided into subcategories of "Vapor Irritant", "Liquid or Solid Irritant", and "Poisons". In Table 4.1, the highest number for any of the subcategories is shown.
- 3) The numbers shown in the column "Rating by Sax" are the highest of any of the subcategories listed by Sax: "Acute Local", "Acute Systemic", "Chronic Local", or "Chronic Systemic". Sax lists lethal doses (mg/kg) for some materials, but these generally relate to ingestion, which would be unlikely by an emergency worker. Therefore, lethal dose values are not included in Table 4.1.
- 4) The EPA category is also listed, where pertinent, in a separate column. These categories are explained in Section 4.2.1.1.

4.4 IR Spectral Data and Interpretation

4.4.1 Introduction

Since identification of hazardous materials by their infrared signatures appears to be the most promising method for instrumentation development (see Sections 5.4 and 6.2.1.2.2), a survey was made of the quality of IR spectra for the materials in Table 4.1. The objectives of this portion of the study were the following:

- 1) To determine which materials have IR spectral peaks in wavelength regions appropriate for detection. This information would shed light on the feasibility of an IR detection scheme in general.
- 2) To specify the wavelength of the principal peak(s) of the materials for which IR spectra exist.
- 3) To determine, where possible, the wavelengths of secondary features in the IR spectra.
- 4) To describe significant qualitative features of the IR spectra. (Copies of spectra of many of the materials in Table 4.1 have been obtained, but reproduction of all of these spectra was deemed too bulky for this report.)

The survey conducted in this part of the study was comprehensive, in the sense that data on all the materials in Table 4.1 were sought. However, within the scope of the present project, the survey was not intended as exhaustive. That is, an attempt was not made to search every possible source of spectral data or to assure that the highest resolution or most recent measurements were used. Thus, a blank in a particular column of the tabular data in this report does not necessarily imply that no information exists.

The principal sources of IR spectral data were The Sadtler Standard Spectra (20), The Coblentz Society Spectra (21), and the Foxboro Analytical listing of "1979 OSHA Concentration Limits for Gases" (22). This information was supplemented for particular materials by data from References 23 through 31.

4.4.2 IR Spectral Data

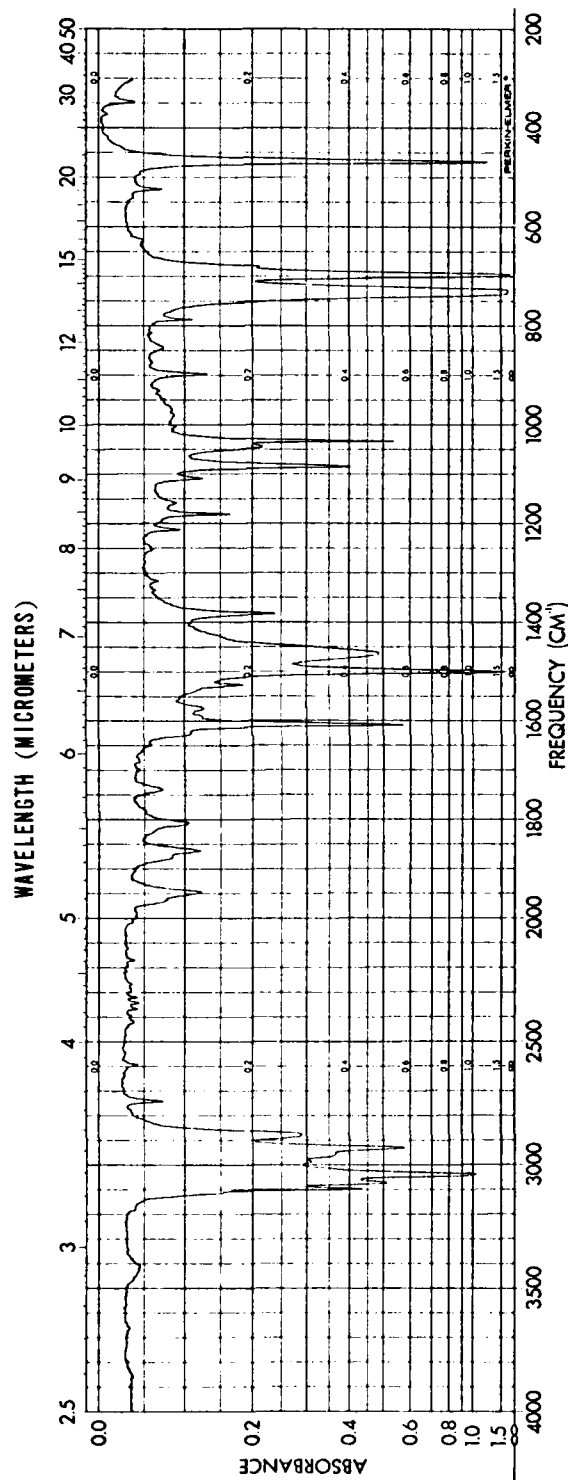
Laboratory measurements of infrared spectra are generally made by passing an IR beam, tunable in wavelength (or frequency), through a sample of a material and measuring the absorption of this beam as a function of wavelength. When the wavelength of

the beam matches quantum vibrational/rotational states in the target material, higher absorption occurs. The series of vibrational/rotational states is characteristic of each molecule, and the spectrum produced uniquely identifies that material.

For illustrative purposes, a typical IR absorption spectrum, for Toluene, is shown in Figure 4.2. The measurement has been made with relatively good resolution, so that the narrow peaks are well resolved. The scales on the chart include wavelength in micrometers (μm) and frequency expressed in wavenumbers or reciprocal centimeters. (To find the frequency in cycles/sec multiply the wave number by the velocity of light in cm/sec.)

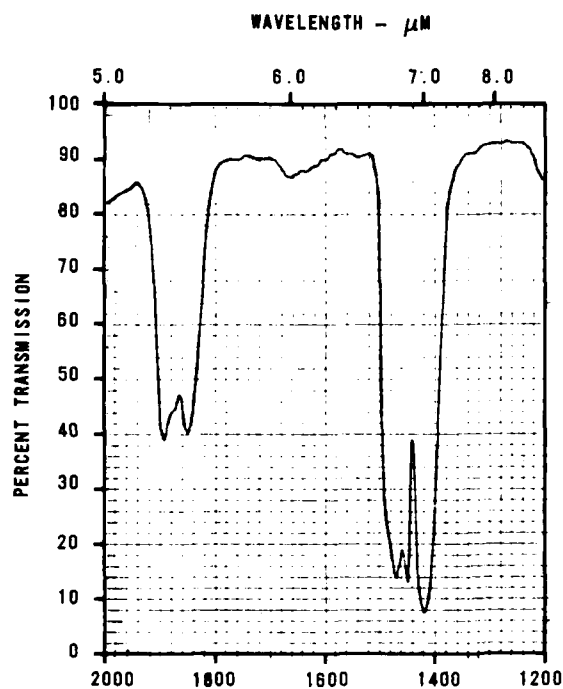
The resolution with which measurements are made has a strong effect on the types of features which show up in a spectrogram. Peaks of narrow width will not appear if measured by an instrument with insufficient resolving power. This feature is illustrated in Figure 4.3 where portions of Sadtler Research Laboratory Spectra of Ethylene measured with two different instruments are shown. As can be seen, for the two bands centered at about 5.4 and 7.0 μm , the prism spectrometer measurement (4.3a) shows double-structured peaks, but does not reveal the narrow central spikes which are resolved by the grating instrument (4.3b). This does not necessarily mean that materials cannot be discriminated with a relatively low resolution instrument; both measurements reveal some features at about 5.4 and 7.0 μm . However, if reference information is used in a discrimination system, and that information has been obtained by an instrument with different resolution (higher or lower) than that of the measuring system itself, serious errors in interpretation could occur. Therefore, it will be important for the development of any hazardous material instrument system that the reference data be compatible with the resolution of the instrument.

A summary of the IR spectral information which was gathered within the scope of this program is presented in Table 4.2. As discussed in Section 5.4, the most promising IR system



F F Fig. 4.2 - Example IR Absorption Spectrum - for Toluene, e
Reference 23, Figure 5-37, used with permission.

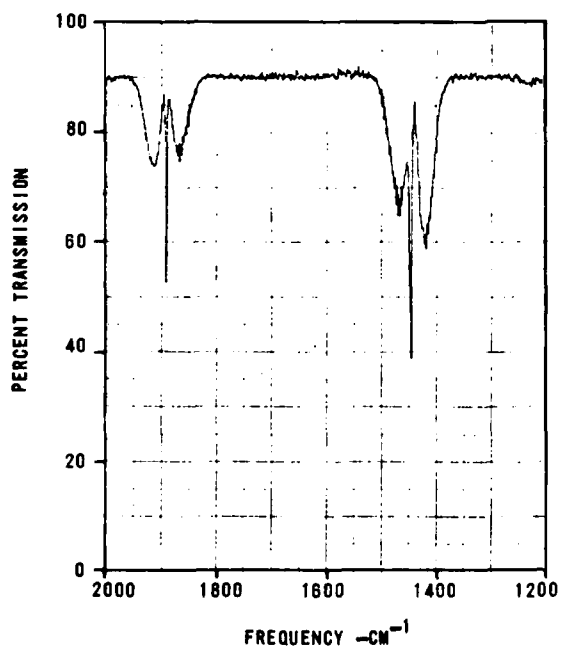
NOTE THAT ABSOLUTE MAGNITUDES OF THE PEAKS ARE DIFFERENT BECAUSE OF DIFFERENT AMOUNTS OF GAS PRESENT.



4.3a Prism Spectrometer
Sadtler Spectrum #1131

CELL: 5 cm

© Sadtler Research Laboratories,
Division of Bio-Rad Laboratories,
INC., 1962



4.3b Grating Spectrometer
Sadtler Spectrum #GS14

SCANNED ON DIGILAB FTS-14
PATH LENGTH: 10 cm
PRESSURE: 70 mm Hg

© Sadtler Research Laboratories,
Division of Bio-Rad Laboratories,
INC., 1972

Fig. 4.3 - Comparison of IR Spectral Features. Portions of the Spectra Measured for the Same Material, Ethylene (C_2H_4), by Two Different Instruments are Shown.

operates in the 8-12 μm range. Therefore, the information in Table 4.2 is divided into data on the 8-12 μm region and data at other wavelengths. Under the heading "Principal λ ", the strongest peak in the 8-12 μm range is identified (if two or more peaks of almost equal intensity exist, they are identified). A brief qualitative description of the shape of the principal peak(s) is then given. These qualitative features may depend to at least some extent on the resolution with which that particular spectrum was measured. In cases where no qualitative description is given, the information cited is based on a numerical value of the wavelength of a particular line, rather than on a complete spectrum.

For the lines at wavelengths outside the 8-12 μm region, asterisks indicate those that would be masked by atmospheric absorption bands. (For more details of the atmospheric absorption spectrum, see Figure 5.2). If a hazardous material detection instrument were operated at relatively short range against a high density or strongly emitting target, it could turn out that some spectral features would not be totally obscured by atmospheric absorption at the same frequencies. If the possibility of extending the wavelength range of an instrument were considered, the discriminability of various substances would have to be determined based on relative densities, ranges, and intensities of spectral lines of the atmosphere and target materials.

Material for which no spectral data is presented in Table 4.2 include symmetrical diatomic molecules or simple atomic substances which are not IR active (see Section 5.4.4 for a further discussion of this aspect), and materials for which spectral data were not found in the sources consulted.

4.4.3 Conclusions

The most important general conclusion from this survey of IR spectral data is that most of the hazardous materials studied show significant spectral features in the 8-12 μm region. Thus, from the point of view of spectral data alone,

Table 4.2 - Principal IR Spectral Lines				
MATERIAL ref.	STATE	LINES IN 8-12 μ m RANGE		LINES AT OTHER WAVELENGTHS
		PRINCIPAL λ (μ m)	QUALITY	OTHER LINES
GROUP 1A				
Sulfuric Acid ²⁴	L	8.6, 10.3	broad	11.1
Oxygen	L/G	- - -	- symmetrical molecule	- - -
Ammonia ²³	G	10.4, 10.8	narrow	9.7, 11.8 fine; may show up as broadband ~9-12
Ethylene ^{20 21}	G	10.5	narrow spike on very broad band	6.2*, narrow; 12.1, 12.3, 12.4
Chlorine	G	- - -	- symmetrical molecule	6.8*, 7.1*; 5.3, 3.3
Sodium Hydroxide	S			
Phosphoric Acid ²⁷	L/S	10.0	broad	6.1*
Nitric Acid ²⁴	L	10.8	broad	12.9, 7.7*, 5.9*, 3.0
Ammonium Nitrate ²⁰	S	11.9, 12.1	narrow; stronger peak at 12.1	7.2*, broad; 5.7*; 3.2, 4.1
Propylene ²¹	G	11.0	narrow spike on broad band	6.9*, 6.0*, 5.5*; 3.4, 3.2
Benzene ²¹	L	9.6	narrow spike on narrow band	14.9, 14.5, 15.2, strong; 6.7*, 5.5*, 5.1, 3.3, 3.4
Ethylene Dichloride ^{20 22}	L	8.1, 11.3	narrow	14.0, 7.8, 7.6*, 7.0*, 6.9*, 3.4
Toluene ²³	L	9.6, 9.2	narrow	13.7, 14.3, 6.7*, etc., 6.2*, 5.1*, etc., 3.3, 3.4, 3.5
Ethylbenzene ²¹	L	9.7, 11.1	narrow	14.3, 13.4, 13.1, 6.7*, 6.9*, 6.2*, 3.4, etc.
Vinyl Chloride ²⁰	G	10.7, 11.2	narrow spike on broad band	13.7, 14.1, 7.7*, 7.9, 7.3*, 6.2*, 6.6*, 5.6*, 3.3
Styrene ²³	L	11.0, 10.1	narrow	14.4, 12.5, 6.7*, etc., 5.5*, 3.3, 3.4
Formaldehyde ^{20 23}	G	8.6	narrow, not strong	7.8, 6.8*, etc., 5.7*, etc., 3.6, 2.8

Table 4.2 - Principal IR Spectral Lines (Cont'd.)				
MATERIAL ref.	STATE	LINES IN 8-12 μ m RANGE		LINES AT OTHER WAVELENGTHS
		PRINCIPAL λ (μ m)	QUALITY	
GROUP 1A (cont'd.)				
Methanol ²¹	L	9.7	narrow spike between 2 broader peaks	7.3*, 6.7*, 4.8, 3.9, 2.7
Xylenes ^{20, 23} m o p	L	9.6 9.5 8.9	narrow	13.0, 6.2*, 6.7*, 3.3 13.5, 6.8*, etc., 3.4 12.6, 6.6*, etc., 3.4
Hydrochloric Acid ²¹	G/L	9.5	broad, weak compared to 3.5	14.3, 3.5 (many high spikes, probably unresolvable)
Ethylene Oxide ²⁰	G	11.5	center of a broad band	7.9, 6.1*, 6.7*, 4.4*, 3.3
Ethylene Glycol ²³	L	9.1, 9.3	double, relatively broad peak	6.9*, 7.1*, 3.0, 3.4, 3.5
Ammonium Sulfate ²¹	S	9.0	broad peak	7.1*, 3.2
Butadiene ²¹	G	11.0	slope on broad peak	7.2*, 6.2*, 5.5*, 3.2, 4.2*
Cumene ²⁰	L	9.7	narrow	13.0, 14.2, 6.7*, etc., 3.4, etc.
Acetic Acid ²⁰	L	10.7	broad	7.8*, 7*, 5.8*, 3.2, etc.
Phenol ²¹	S	8.2	broad	12.3, 13.3, 14.5, 6.3*, etc., 3.0, 3.3, 2.8
Cyclohexane ²⁰	L	11.6	relatively narrow	12.6, 7.9, 6.9*, 4.3*, 3.5
Acetone ²⁰	L	8.2	relatively narrow	13.0, 7.4*, 7.0*, 5.8*, 3.3
Propylene Oxide ²⁰	L	12.0	slope on broad peak	13.0, 13.2, 7.1*, 7.9*, 3.4
Acrylonitrile ²⁰	L	10.4	relatively broad; well-defined	14.5, 12.5, 7.1*, 6.2*, 5.2*, 4.5, 3.3

Table 4.2 - Principal IR Spectral Lines (Cont'd.)					
MATERIAL ref.	STATE	LINES IN 8-12 μ m RANGE			LINES AT OTHER WAVELENGTHS
		PRINCIPAL λ (μ m)	QUALITY	OTHER LINES	
GROUP 1A (Cont'd.)					
Isopropanol ²¹	L	8.7, 10.5	relatively broad, well-defined	9.3, 8.0 relatively broad	12.3, 13.3, 7.2*, 6.7*, 3.3, 3.5
Vinyl Acetate ²⁰	L/S	8.2, 8.8	relatively broad, well-defined	9.8, 10.5, 11.4, 10.3, 11.8 relatively broad	7.3*, 6.1*, 5.7*
Acetic Anhydride ²⁰	L	8.9	relatively broad, well-defined	10.0, 11.1, 8.1, 9.5 relatively broad	12.6, 12.4, 7.0*, 5.5*, 3.3
Ethanol ²⁰	L	9.5, 9.2	parts of double peak	11.3, relatively narrow	12.4, 7.2*, etc., 3.0, 3.4

Table 4.2 - Principal IR Spectral Lines (Cont'd.)				
MATERIAL ref.	STATE	LINES IN 8-12 μ m RANGE		LINES AT OTHER WAVELENGTHS
		PRINCIPAL λ (μ m)	QUALITY	OTHER LINES
GROUP 1B				
Gasoline	L		mixture of heptane, octane, etc.; identifiable by these components	
Kerosene	L		mixture of nonane, decane, etc.; identifiable by these components	
Fuel Oils	L		mixtures; identifiable by components	
Ethane ²⁰	G	12.0	broad peak extending beyond 12 μ m	6.8*, 3.4, 3.6
Propane ²¹	G/L	10.8	sharp spike on broad peak	13.4, 7.5*, 7.3*, 6.8*, 3.4
Butane ²⁰	G/L	10.3	broad peak	13.3, 13.6, 7.7*, 7.2*, 6.8*, 3.4
Isopentane ²⁰	L	8.8	broad	13.1, 7.3*, 6.8*, 3.4
Isobutane ²⁰	G/L	8.5	narrow	12.7, 7.5*, 7.3*, 6.8*, 3.8, 3.5
Pentane ²⁰	L	11.3, 9.4	broad peaks of multiple spikes	13.8, 13.2, 12.6, 12.2, 7.3*, 6.8*, 3.5
Hexane ²⁰	L	11.0, 11.6	relatively broad	13.1, 13.6, 7.9*, etc., 7.3*, 6.9*, 3.5
Heptane ²⁰	L	10.8	broad	13.1, 13.9, 12.1, 7.3*, 6.9*, 3.5
Octane ²⁰	L	11.4, 9.3	relatively broad	13.9, 13.1, 7.3*, etc., 6.9*, 3.5
Natural Gas ²⁰	G/L		a large portion methane	
Acetylene ²⁰	G	none on scale of graph		13.6, spike on broad peak; 7.4*, 7.7*, 3.1

Table 4.2 - Principal IR Spectral Lines (Cont'd.)					
MATERIAL REF.	STATE	LINES IN 8-12 μ m RANGE			LINES AT OTHER WAVELENGTHS
		PRINCIPAL λ (μ m)	QUALITY	OTHER LINES	
GROUP 11					
Acrolein ²¹	L	10.4, 8.6	spike on broader peak	10.9, 10.1, 11.1, 8.7 other spikes on broad peaks	16.7, 13.7, 7.1*, 5.8*, 3.6, 3.2, 2.9
Boron Trifluoride ²¹	G	10.6	spike on broader peak	11.0, 10.7, 9.8	14.0, 12.2, 6.9*, 6.7*, 4.3*, 3.4
Bromine	L	- - -	symmetrical molecule	- - -	
Carbon Disulfide ²⁰	L	11.7	broad	none	6.7*, 4.7, 4.4*, 3.6
Dimethyl Ether ²⁰	G	8.4, 8.5	broad structure	9.0, 9.1 (pair), 10.7, 10.9 (pair)	6.9*, 7.1*, 3.5
Dimethyl Sulfate ²⁰	L	8.3, 9.9, 10.1	relatively broad	none	12.1, 13.2, 7.2*, 6.9*, 3.4
Epichlorohydrin ²⁰	L	11.7, 10.8	relatively broad	10.4, 11.0, 9.1, 8.8, 8.4	13.1, 13.8, 7.9, 7.1*, 6.9*, 3.4
Ethyl Chloride ²⁰	L	10.1, 10.4	features on same band	10.3	12.7, 14.6, 7.7*, 7.8*, 7.1, 6.9 3.4
Ethyleneimine ²⁰	L	11.7	broad	10.8, 9.9, 9.2, 8.3 broad	12.8, 13.8, 7.9, 7.4*, 6.9*, 3.1 etc.
Fluorine	G	- - -	symmetrical molecule	- - -	
Hydrogen ^{22, 25, 26, 29}	G/L	- - -	symmetrical molecule	- - -	
Hydrogen Cyanide ^{30, 31}	G	8.6, 8.8	very weak	-	14.1, 4.8, 4.5, 3.04
Hydrogen Fluoride ²¹	G/L	10.4	broad	8.3	3.3, 2.9, 2.5
Hydrogen Sulfide ²¹	G	8.0	band of narrow spikes	8.2, 8.3, 8.5, 8.9, etc.	7.7*, 7.4*, 3.7
Methane ²⁰	G/L	8.0	band of spikes centered at 7.7	8.1, 8.2, 8.6	15, 7.7*, 7.4*, 3.3, 2.4
Methylamines ²⁰ di-	G	8.7, 9.7	broad	10.7, 10.9	13.8, 6.8*, 3.5
tri-		9.6, 12.1	broad	11.8, 9.0, 8.4	7.8*, 6.8*, 3.4, 3.6
Methyl Bromide ²⁰	L	10.4	spikes on broad peaks	10.2, 10.7, etc., 8.5	7.6*, 7.7*, 7.0*, 3.4

Table 4.2 - Principal IR Spectral Lines (Cont'd.)					
MATERIAL REF.	STATE	LINES IN 8-12 μ m RANGE			LINES AT OTHER WAVELENGTHS
		PRINCIPAL λ (μ m)	QUALITY	OTHER LINES	
Methyl Chloride ^{20, 22, 25}	G	9.9	many sharp spikes closely spaced, centered at 9.9 μ m	none	13.4, 13.5, 14.0, 7.4* etc., 3.5
Methyl Ethyl Ether	G/L	9.4	broad	9.2, 10.0, 10.5	13.8, 14.1, 14.4, 7.4*, 7.6*, 6.9*, etc., 3.4
Methyl Mercaptan ²⁰	G/L	-		-	12.4, 13.4, 14.8, 7.9, 7.2*, 5.4*, 5.7*
Nitrogen Tetroxide ²⁶	G	11.8	relatively narrow	9.9, 8.6, 8.7	15.0, 7.1*, 6.0*, 5.5*, 4.3*, 2.8*
Phosgene ²¹	G	-		-	19.5
Phosphorus Tri- ²⁵ s chloride	L	8.6, 8.8	double spikes on broad peak	none	7.3*, 7.4*, 4.0
Sulfur Dioxide ²⁰	G	-		-	19.8
Titanium Tetrachloride ²⁶	L	-		-	

Table 4.2 - Principal IR Spectral Lines (Cont'd.)

MATERIAL REF.	STATE	LINES IN 8-12 μ m RANGE		LINES AT OTHER WAVELENGTHS	
		PRINCIPAL λ (μ m)	QUALITY	OTHER LINES	*Indicates obscured by atmospheric bands
GROUP III					
Chlorosulfonic Acid ²⁰	L	8.5, 10.9	broad	none	15.8, 7.2*, 4.1, 3.3
Phosphorus	S	-		-	
Pentasulfide	L	-			14.1, 4.8, 4.5, 3.04 (HCN)
Acetone Cyano- hydrin ^{22 25 26}	L				
Isoprene ²⁰	L	11.2, 10.0	11.2 - broad 10.0 - narrow	9.3, 10.5	13.1, 6.9*, etc., 6.2*, 5.6*, 3.4, 3.3
DDT ²⁰	S	9.1	relatively broad	9.0, 12.0, 11.8, 9.8, 10.0	12.8, 13.0, 41.1, 13.7, 12.4, 6.7* etc., 3.5
Cyclic Rodentici- des (Aldrin) ²⁰	S/L	9.6, 11.1	spikes on broad peaks	10.9, 11.2, 12.0, 9.3, 8.5	12.3, 12.9, 14.0, 14.4, 7.9, 7.5*, 3.3
Cyclic Insecti- cides (Endrin) ²⁰	S/L	11.8	Narrow	11.3, 9.6, 9.9, 10.2, 9.3, 8.5, etc.	13.4, 14.0, 14.7, 12.5, 7.9, 7.7* etc., 3.4, 3.0
Sulfur ²⁶	S/L	-		-	15.0 (crystalline form)
Calcium Fluoride	S	-		-	-
Calcium Carbide	S				
Acetaldehyde ²⁰	L	8.9, 9.1	double spikes on broad peak	10.7, 10.9, 11.5, 11.7	13.1, 7.3*, etc., 5.7*, 3.6
Butenes ²³ Cis-2	G	10.2	relatively broad	9.3, 11.4	14.8, 6.9*, etc., 6.0*, 5.0*, 3.4
Trans-2		10.4, 9.4	broad	8.9	14.8, 6.9*, etc., 5.9*, 5.0*, 3.4
Iso-		11.8, 9.4	broad	10.3, 8.9	12.4, 7.8*, 6.9* etc., 6.0* etc., 3.4
Phosphorus ²⁶	S	-		-	15.8 (P ₄ crystal)
Carbon Tetra- ²⁰ chloride	L	10, 10.2	broad	8.0, 8.2	12.8, 13.2, 6.5*
Napthalene ²⁰	S	10.5, 8.9	narrow	10.0, 11.9, 8.3, 8.1, 8.8, 10.2	12.8, 13.4, 12.2, 7.9, 7.2*, etc., 3.4
Perchloroethylene ²¹	L	11.0	narrow	10.1, 8.9, 9.1, broad	13.1, 12.5, 13.2, 7.4*, 6.4*

Table 4.2 - Principal IR Spectral Lines (Cont'd.)					
MATERIAL REF	STATE	LINES IN 8-12 μ m RANGE			LINES AT OTHER WAVELENGTHS
		PRINCIPAL λ (μ m)	QUALITY	OTHER LINES	
Propyl Alcohol ²⁰	L	9.4, 10.3	narrow	9.3, 9.8, 9.1, 11.0, 11.2, 11.6, 8.1	13.2, 6.8*, etc., 3.0, 3.4, 3.5
Trichloroethylene ²⁰	L	11.9, 10.6	relatively narrow	-	12.8, 3.2
Tetraethyl Lead ²¹	L	-	-	-	-
Methyl Ethyl Ketone ²¹	L	8.6	relatively narrow	10.6, 10.1, 9.2, 8.3, 8.0	13.2, 15.3, 7.4*, etc., 5.8*
Methyl Methacrylate	L	8.6, 8.3	double spikes on broad peak	10.6, 9.8, 9.3	12.3, 12.5, 15.5, 7.5*, etc., 5.7*, 3.4
Aniline ²⁰	L	8.5, 11.3	relatively narrow	10.0, 9.7, 9.5, 8.6	13.2, 14.4, 7.8*, 6.2*, etc., 3.0, 3.3
Butyl Alcohol ²³ n-	L	9.4, 9.6	spikes on relatively broad peak	10.3, 11.8, 9.0, 8.2	13.6, 15.5, 6.8*, etc., 3.4, 3.0
sec-		10.1, 11.0	relatively narrow	9.6, 8.9, 8.7, 10.4	12.2, 12.8, 16.0, 7.2*, etc., 3.4, 3.0
tert-		8.3, 10.5	relatively narrow	9.8, 8.1	13.4, 16.0, 7.3*, etc., 3.4, 3.0
Potassium Hydroxide ^{20, 22}	S	-	-	-	-
Trichloroethane	L	9.2	narrow	8.9, 11.4, 11.3	14.0, 7.9, 7.2*, 6.9*, 3.4
Ethanolamine ²⁰	L	9.6	broad	9.3, 10.4, 11.5, 8.5, 8.1, broad	7.4*, 6.8*, 6.3*, 3.1, 3.5
Aluminum Fluoride ²⁴	S	11.7	very broad	8.3, 9.8, 9.0, very broad	14.4, 5.9*, 3.2, 3.9
Perchloric Acid ²⁸	L	9.6	relatively narrow	8.2, broad	13.4, 7.6*
Maleic Anhydride ²⁰	S	12.0, 11.2, 9.5	narrow	11.5, 8.1 narrow	14.5, 7.9, 7.8*, 5.6*, 3.0, 3.2
Sodium	S	Simple Element	-	-	-
Turpentine ²²	L	-	-	-	3.4
Isopropyl Acetone	L	-	-	-	-
Ethyl Acetate ²¹	L	8.1, 9.5	relatively narrow	9.1, 10.7, 11.8	12.7, 16.0, 7.7*, 7.3*, 5.7*, 3.3
Nonene ²⁰ 1-	L	11.0, 10.1	relatively narrow	8.3, broad	13.8, 7.8*, 7.3*, 3.4
4-	L	10.3	relatively narrow	9.1, 9.4, 10.8, 11.2, broad	13.5, 7.2*, 6.8*, 3.4

Table 4.2 - Principal IR Spectral Lines (Cont'd.)

MATERIAL ref.	STATE	LINES IN 8-12 μ m RANGE		OTHER LINES	LINES AT OTHER WAVELENGTHS
		PRINCIPAL λ (μ m)	QUALITY		
Chlorobenzene ^{20 22}	L	9.2	narrow	9.8, 8.9, 9.4, 10.4, 11.1	13.5, 14.4, 14.6, 6.7* etc., 3.2
Chloroform ²⁰	L	8.2	narrow	none on scale of graph	13.1, 3.4
Barium Carbonate ²⁰	S	11.7	narrow	9.5, 12.0, narrow	14.5, 7.0*, 5.7*, 4.1
Tetramethyl Lead	L	-		-	-
Dichlorobenzene ²⁰	L/S	9.7	narrow	8.0, 8.9, 10.6	13.4, 6.8*, 6.9*, 6.3*, 3.2
Dinitro-Aniline		-		-	-
Ammonium Per-chlorate ^{21 25}		9.4	very broad	10.7, small, broad	7.0*, 3.03, 3.0

the potential for using the 8-12 μm "window" for discrimination of hazardous materials is encouraging.

Of the 100 materials for which some spectral information was available, 92 were determined to have spectral features to allow potential discrimination over the 8-12 μm range. Not only do many materials have major peaks in this range, but most also show multiple secondary peaks to allow discrimination where the major peak may coincide with that of another material. Several materials without strong peaks in the 8-12 μm range, for example acetylene and hydrogen chloride, would be detectable by an instrument sensitive to a wider range of wavelengths. The materials causing the greatest problems are the symmetrical diatomic molecules, which are not infrared active. Such materials would need to be handled by means other than discrimination by IR spectra, as discussed in Section 5.4.4.

5.0 REMOTE SENSING METHODS FOR IDENTIFYING MATERIALS

5.1 Introduction

5.1.1 Overview

Since the advent of the laser in 1961, a great deal of research has been performed on remote sensing techniques for the measurement of gaseous and particulate matter in the atmosphere.* The great advantage of remote sensing is that it permits the monitoring of specific components of a gaseous body without coming into direct contact with that body. Clearly, this would be a desirable characteristic for detecting and monitoring gaseous bodies of hazardous materials. A summary of the more successful remote sensing systems is presented in Section 5.2, and a comparison of the systems is given in Section 5.3.

It should be noted that remote sensing techniques as applied to atmospheric observations, particularly pollution monitoring, differ in several fundamental ways from techniques as they would be applied to the hazardous material problem. All of the systems described in Section 5.2 have been applied only to atmospheric observations. They have been operated by highly-skilled operators, and have been applied to the precise measurement of low-level concentrations of, at most, a few pre-determined species of molecules. None of the systems has yet been applied to the problem of determining which, if any, of a large number of possible species is present. Nevertheless, the great body of research which has already been performed on remote sensing techniques for atmospheric observations is very useful. It has led to the development of the components which may be utilized for the remote sensing of hazardous materials. A proposed remote-sensing system which may adequately indicate the presence of a hazardous material and simultaneously identify it is described in Section 5.4.

*A bibliography of most of the pertinent publications may be obtained from the references at the end of the review-type publications listed as References 32-35.

5.1.2 Technical Introduction

5.1.2.1 General System Characteristics

When a particular species of gaseous molecule is illuminated by a variable frequency light* source, an absorption spectrum can be observed which is characteristic of that species of molecule. Similarly, when the gaseous molecules are excited by heat or external light sources, they emit a radiation spectrum which is similar (though not necessarily identical) (36) to the absorption spectrum. This spectrum is again characteristic of that particular species of molecule. The detection and measurement of a specific species of gaseous molecule is based upon the fact that all gaseous molecules have such characteristic spectra. Some remote sensing systems utilize the radiation of one or a few characteristic strong spectral lines, while other systems measure the complete spectrum for a broad band of frequencies (or wavelengths) (32-35). Details of the more successful remote sensing systems are described in Section 5.2.

In order to observe a spectrum, it is necessary to have a light source. This source can be used in an absorption measurement mode in some systems, or as an exciter in others. If this light source is natural, such as sunlight or blackbody infrared radiation from terrain, then the system is called a passive system. If, however, a non-natural external light source such as a laser or a lamp is utilized, then the system is called an active system. Active systems may be further subdivided into double-ended and single-ended systems. In a single-ended system, the external source and the detector are at the same location (often housed in the same container); while for a double-ended system, they are separated. Active systems include lidar systems wherein a pulse laser source generates a density versus distance profile of a gas using radar signal processing techniques.

*The term "light" as used in this report refers to electromagnetic radiation in general and, as such, includes infrared, visible, and ultraviolet radiation.

Passive infrared systems utilize blackbody (thermal) radiation. In order for this type of system to function properly, it is necessary for the field-of-view to contain at least two objects at different temperatures (37). Passive systems have some obvious advantages in military environments, and many of the developments in this area have been achieved under DoD contracts. Fortunately, not all of the literature in this area is classified. Several system components which have been developed in this research will be key parts of the potential hazardous material identification system described in Section 5.4.

5.1.2.2 Detection Systems

Block diagrams of two types of detection systems are shown in Figures 5.1a and 5.1b. The detection set-up shown in Figure 5.1a is more commonly employed, and it yields an almost immediate result. The optical part of Figure 5.1a can be a fixed frequency filter in those experiments that emphasize the response of a particular spectral line, or it can be a variable filter system such as a monochromator. In all cases, the filters must be narrow-band to obtain the best spectral resolution and simultaneously minimize background radiation. Multi-layer dielectric coatings can be utilized to obtain narrow-band fixed filters and, when applied in a wedge configuration, can serve as a variable frequency filter (37, 35, Section 4.4.6). The best resolution monochromators, though, employ either gratings or Fabry-Perot etalons, and this type of equipment often requires skilled operators.

The detection system shown in Figure 5.1b differs from the preceding system by the use of an interferometer instead of an optical filter. The combination of interferometer and detector yields the autocorrelation function (38) of input radiation, and the Fourier Transform computer yields the spectrum as its output. In this system, an interferogram must be recorded first, then followed up by the Fourier Transform calculation. (The possibility of avoiding the Fourier Transform step is discussed in Section 5.4.3.) It would seem that the interferometer-based detection system is much slower than the monochromator-based system; but this is not necessarily the case. The optical signal throughput

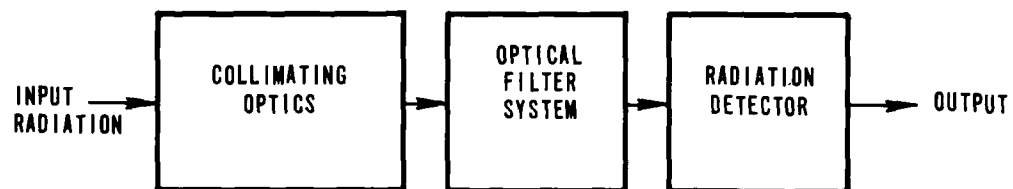


Fig. 5.1a - Detection with an Optical System

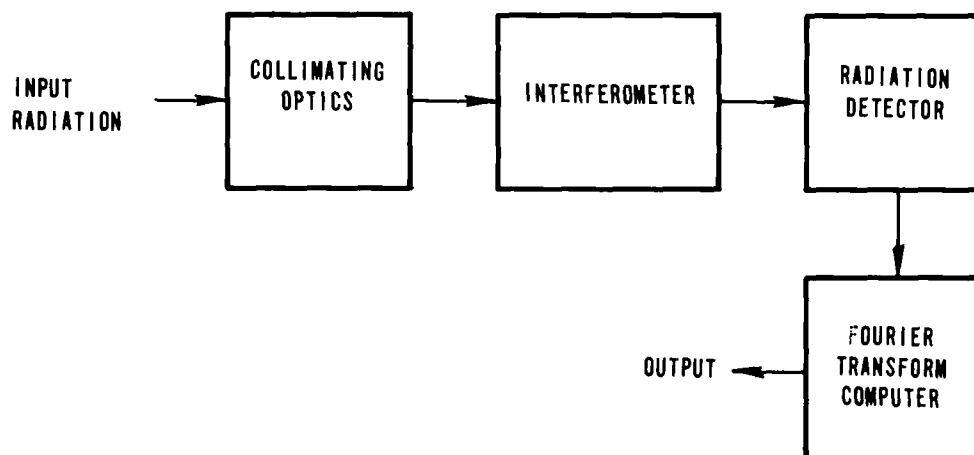


Fig. 5.1b - Detection System with Interferometer

to the detector is much stronger in the interferometer system (Figure 5.1b) than in the monochromator system (Figure 5.1a). A given signal-to-noise ratio at the output of the detector is achieved much more rapidly by the system shown in Figure 5.1b (see Reference 38 for a more detailed description of this phenomenon). Secondly, with "Fast Fourier Transform" procedures and microcomputer technology, the operator of the system can rapidly and inexpensively perform the required calculations. In fact, the presence of a dedicated computer in the system of Figure 5.1b is one of its major operational advantages.

5.1.2.3 Detection Bands

The wavelength (or frequency) region of the spectrum to be measured greatly affects the design of the remote sensing system. Those systems that operate at wavelengths shorter than $\sim 1 \mu\text{m}$ (which includes a part of the near infrared and all of the visible and ultraviolet portions of the spectrum) can utilize photomultipliers as detectors. These detectors can approach the theoretical sensitivity limits predicted by quantum-noise analyses. The large gain of these devices also negates the effects of thermal noise and, in most applications, it is not necessary to cool the photomultiplier tubes (PMT). Detectors which operate at wavelengths longer than $\sim 1 \mu\text{m}$ are either thermal detectors or varieties of photodetectors. The most sensitive detectors in this infrared portion of the spectrum are semiconductor diodes; however, these detectors must be cooled to liquid nitrogen temperatures ($\sim 77^\circ\text{K}$). At present there are no photomultipliers which operate in this portion of the spectrum.

Most gaseous molecules have significant spectral components in the $8 \mu\text{m}$ to $12 \mu\text{m}$ range, as discussed in Section 4.4.2. This portion of the infrared spectrum coincides with a well-known window in the atmosphere (37; 34, p. 318) where absorption by the natural constituents of the atmosphere is relatively weak. There are other windows (34, p. 318) in the middle and near infrared regions, but these are narrower in extent. Furthermore, not as great a variety of substances have spectral components in these

windows as in the 8-12 μm window. A spectrogram illustrating these atmospheric windows is shown in Figure 5.2.

Many of the atmospheric measurements to date have been made using the visible and near ultraviolet portions of the spectrum. This is due to the detector advantages mentioned earlier, and to the availability of a great variety of lasers in this spectral region. These systems are invariably operated by highly-trained personnel, one reason being that the eye-safety problem is a major concern. While all laser systems must take into account eye safety, visible light and near ultraviolet radiation are particularly dangerous (34, Section 6.4.7).

5.2 Current Remote Sensing Techniques

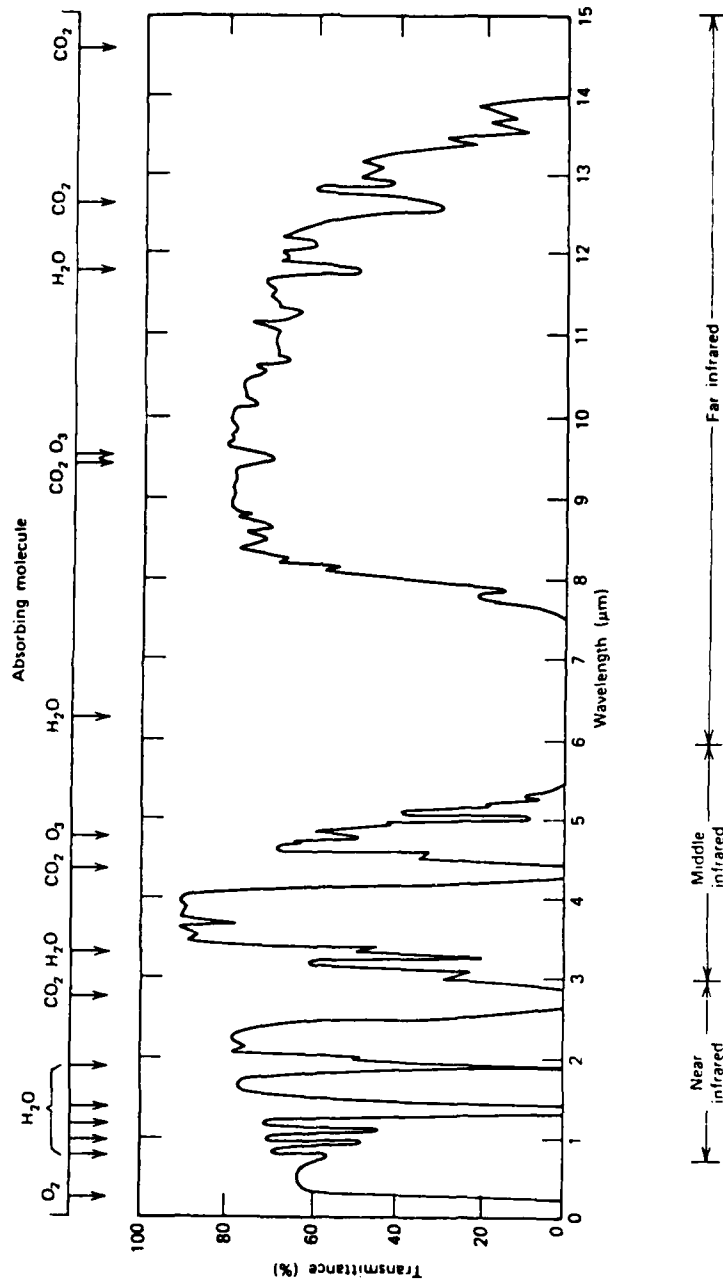
This section discusses the principal applications of remote sensing in pollution monitoring, atmospheric studies, space exploration, and chemical warfare. The possible extension of these instrumentation techniques to the detection of hazardous materials will be explored to the extent warranted by each technique, with comments on attractive features and problem areas.

A number of active techniques, many of which use lasers as sources, are reviewed. Then several passive systems are discussed.

5.2.1 Active Techniques

5.2.1.1 Direct Absorption

In principle, the most straightforward and simple means to remotely identify an unknown material would be to employ a scheme similar to that shown in Figure 5.3. In such a scheme, radiation passing through the target material would be absorbed in a pattern characteristic of that material, and be recorded by a detector system, thus allowing identification. In this scheme, the radiation source might be some broad-band emitter such as an incandescent lamp, or a narrow-band emitter such as a laser, which could be tuned over a certain frequency range. A laser source has the advantage that its radiation is virtually monochromatic,



PATH LENGTH 1828 M, HORIZONTAL PATH AT SEA LEVEL

Fig. 5.2 - IR Transmittance Through the Earth's Atmosphere,
Reference 39, used with permission

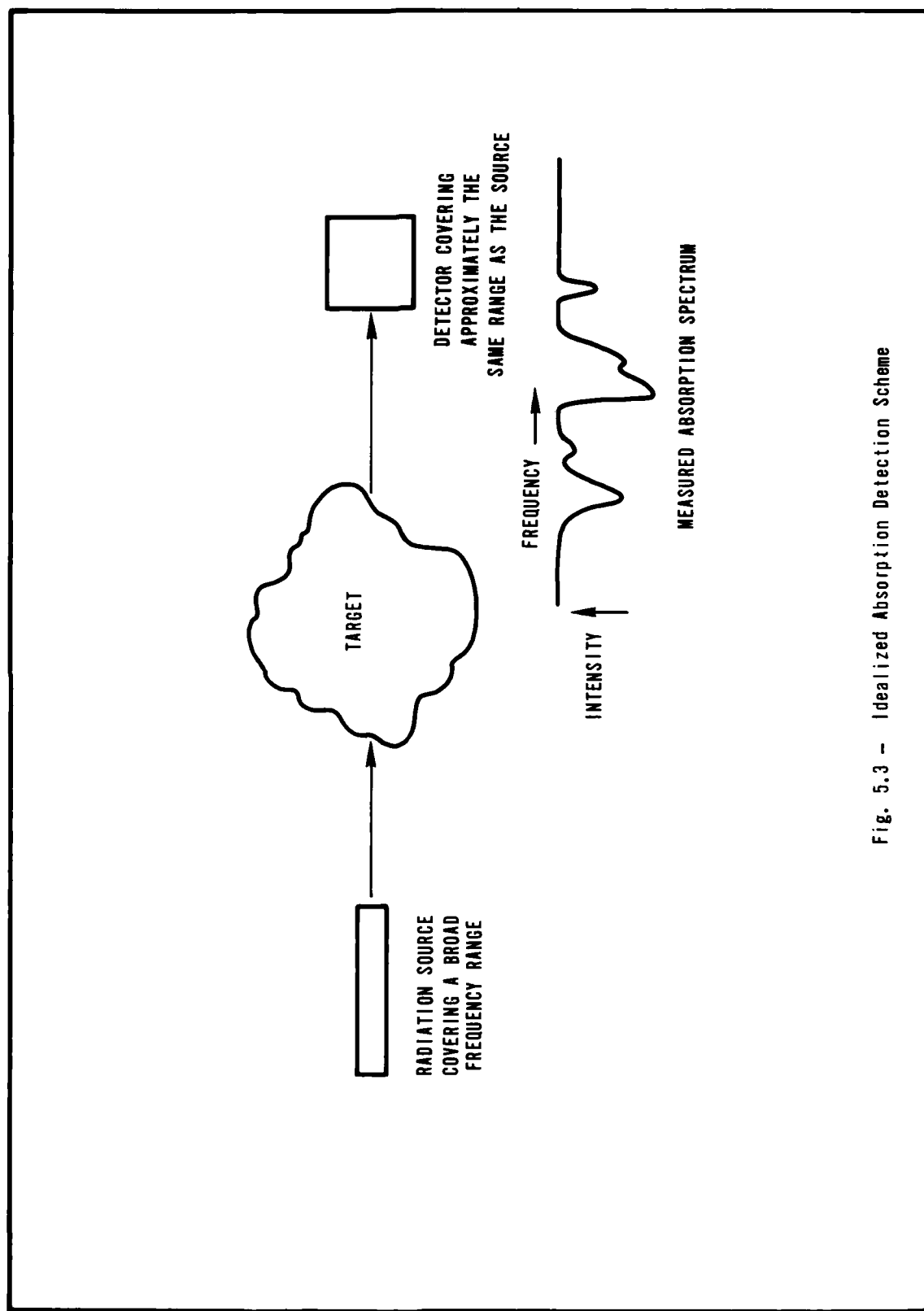


Fig. 5.3 - Idealized Absorption Detection Scheme

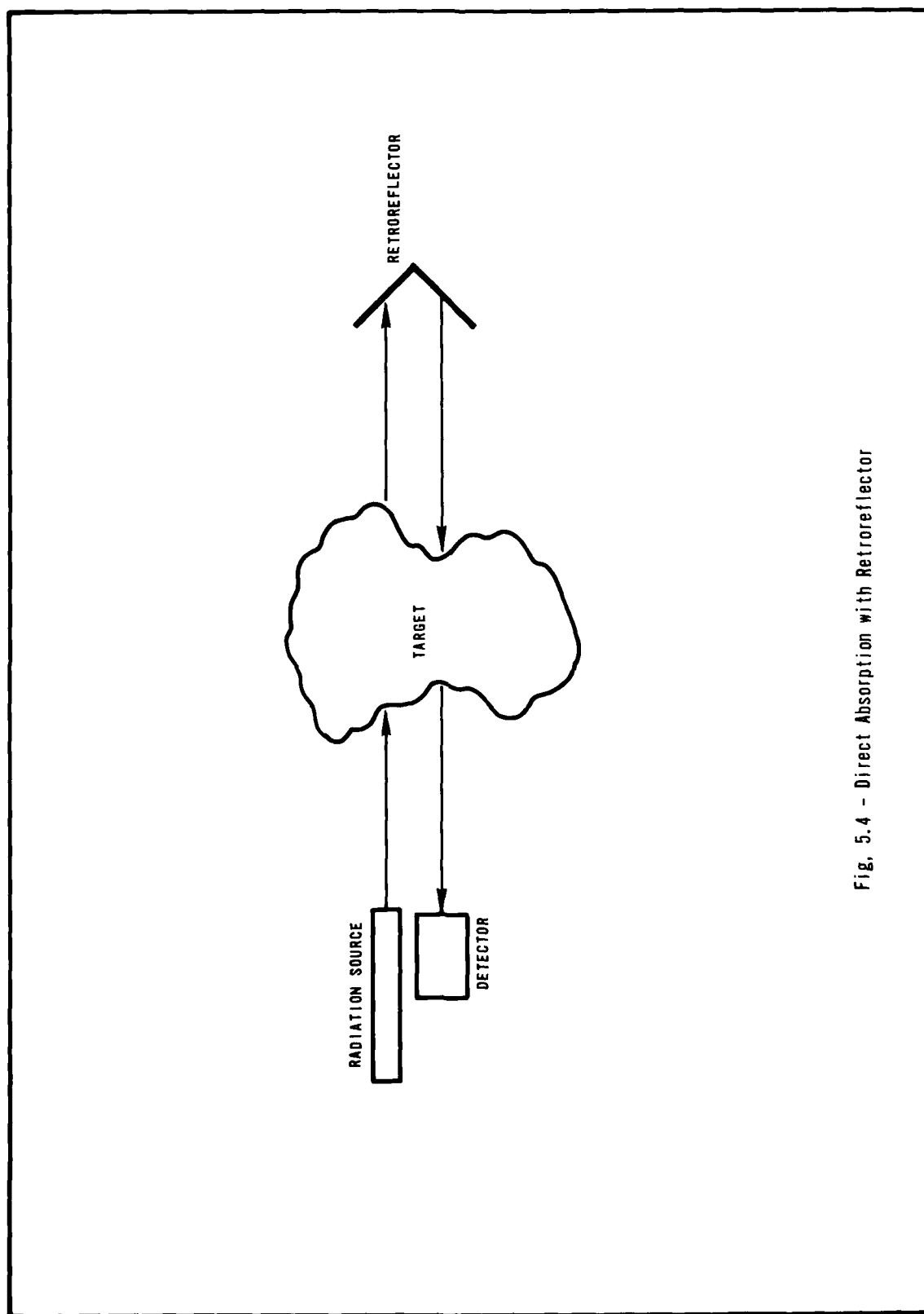
allowing high resolution measurements and easing detector sensitivity over a given narrow frequency interval. The practical problems of broadly tunable lasers are, however, significant, as discussed in Sections 5.2.1.2 and 5.4.5.

A direct absorption scheme will always be basically double-ended. In practice, instead of having the radiation source and detector on opposite sides of the target, a retroreflector is often used, as indicated in Figure 5.4, allowing the source and detector to be contiguous or housed in the same unit. This arrangement still requires something to be placed on the other side of the target, so it is in a sense double-ended. A double-ended system might be better than none at all in emergency situations, but the need to place a source or retroreflector on the opposite side of the target has obvious serious drawbacks for the first-on-the-scene emergency crew. For later, intermediate-time response, a double-ended system would be less objectionable.

Examples of two working systems based on direct absorption are the General Electric ILAMS (Infrared Laser Atmospheric Monitoring System (40)), and EPA ROSE (Remote Optical Sensing of Emissions) system (41).

A schematic of the GE ILAMS System is shown in Figure 5.5. In this design, the initial laser beam is split to provide a reference signal against which the reflected signal attenuated by the atmosphere is compared to yield information on pollutant concentrations.

The CO₂ laser, described as a "multi-wavelength tunable" laser, is designed to provide discrete wavelengths selected from the 74 available in the middle infrared region from a laser using the C¹² and O¹⁶ isotopes. Though 74 is a relatively large number, the lines available still represent a less than continuous portion of the spectral range, and the application of this laser to a large number of hazardous materials would be severely limited. The GE Study suggests the possibility of other isotopes of CO₂ to increase the number of laser lines available, an option possible in the laboratory but infeasible in a field instrument. There also remains the problem of this being a double-ended system.



Fig, 5.4 - Direct Absorption with Retroreflector

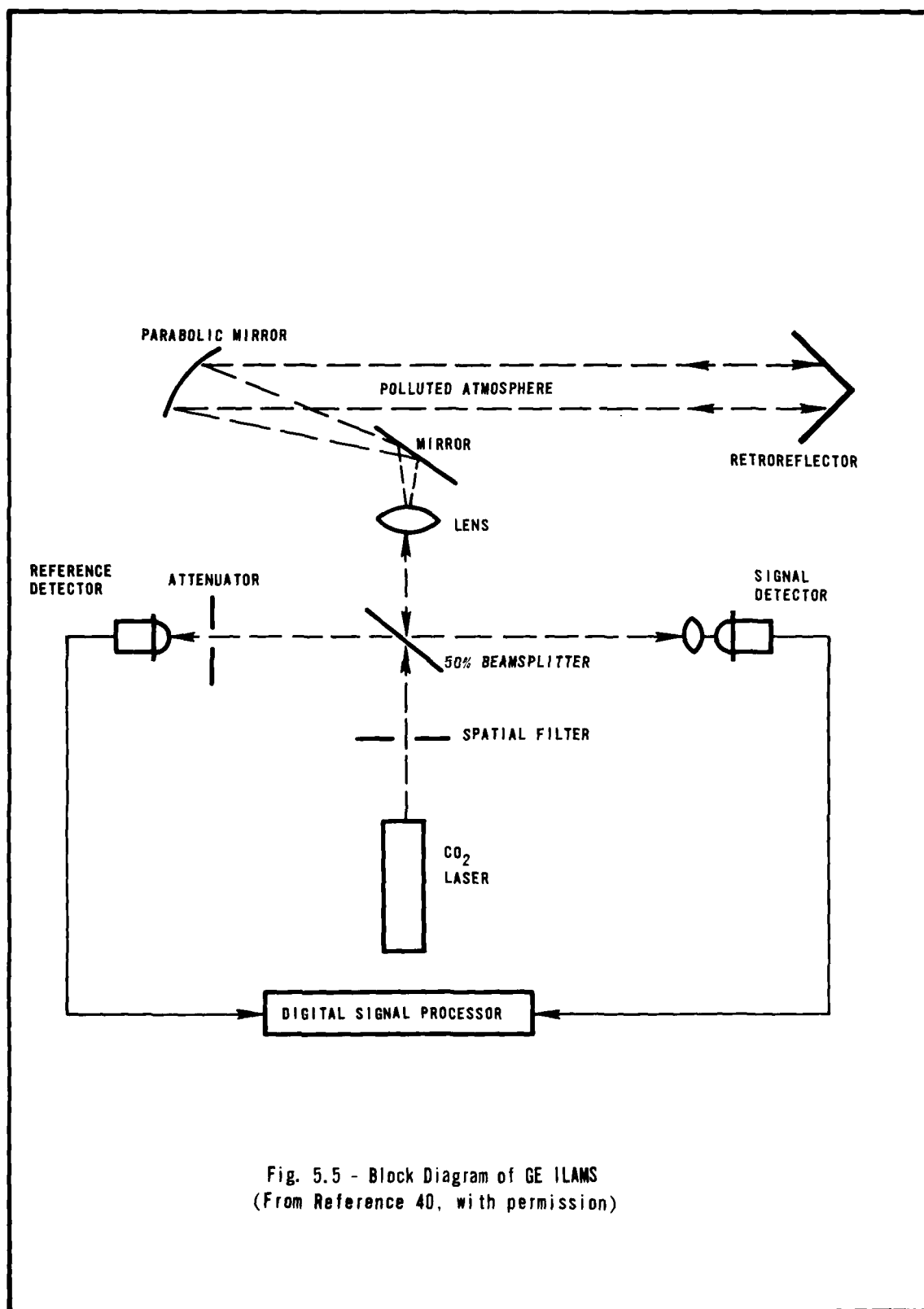


Fig. 5.5 - Block Diagram of GE ILAMS
(From Reference 40, with permission)

The EPA ROSE system was designed and built by General Dynamics/Convair and is operated by the EPA Environmental Sciences Research Laboratory based at Research Triangle Park, North Carolina. The system is mobile to the extent of being installed in an 8.5 meter van. While far from being portable, a system of this size might have some application for intermediate-time response.

An early version of the ROSE system had a blackbody radiation source and a monochromator; but because of signal-to-noise ratio limitations, it could achieve only coarse resolution. The system was modified to use a 1000-Watt quartz-iodine lamp as the source, with its light focused by a Dall-Kirkham telescope through the target material onto an interferometer. The interferometer is part of a moderately high resolution commercial FT-IR (Fourier Transform - Infrared) system, Model 7199, manufactured by the Nicolet Instrument Corporation. Liquid nitrogen cooled HgCdTe and InSb detectors are used for the 600 to 1800 cm^{-1} and 1800 to 6000 cm^{-1} spectral regions, respectively.

A simplified schematic of the ROSE optical system is shown in Figure 5.6. The total system also includes recording hardware and a computer to perform the Fourier analysis. This system is designed to operate in either an absorption mode or an emission mode, collecting radiation from hot stack plumes or jet engine exhausts (this latter technique will be discussed further in Section 5.2.2).

The ROSE system has been used to measure a variety of pollutants in the 1-10 parts-per-billion range over distances of 1 km. It should be emphasized that the system was designed to make quantitative measurements of small amounts of pollutants; it is thus more sophisticated than might be needed for early identification of hazardous materials. However, the system has the attractive feature of not being limited to a specific material or group of materials, but can sense any IR absorber/emitter.

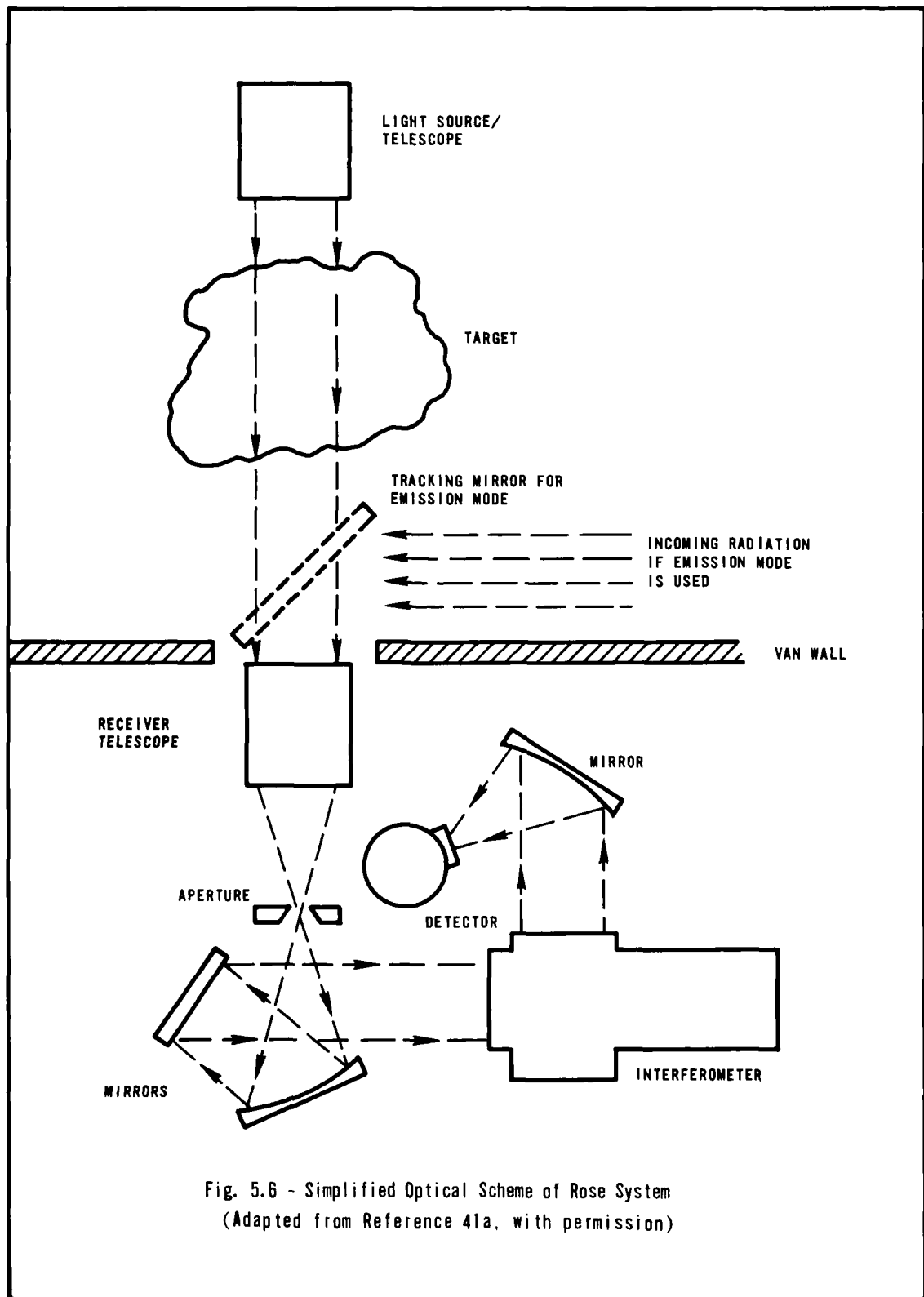


Fig. 5.6 - Simplified Optical Scheme of Rose System
(Adapted from Reference 41a, with permission)

5.2.1.2 Differential Absorption

For applications of remote sensing to pollution measurements where a single known pollutant is to be monitored, a technique called differential absorption has been devised (35, pp. 299-301). In place of a radiation source covering a broad frequency range, two discrete laser frequencies are used, one coinciding with a region of strong absorption in the target materials, the other selected to be "off-resonance," as shown in Figure 5.7. It is assumed that the two frequencies are close enough together that scattering by materials in the atmosphere other than the target material will be the same.

As with direct absorption, in place of having the source and detector on opposite sides of the target, a retroreflector can be used. Menzies and Shumate have described an application of differential absorption for atmospheric studies, developed by the Jet Propulsion Laboratory, using the earth as a retro-reflector (42). In this scheme, the laser and detector equipment are flown in an airplane, and a downward-pointing laser beam, tuned to two different frequencies, is passed through the atmosphere with a portion of the beam being scattered off the earth's surface and detected.

In an attempt to make a differential absorption scheme truly single-ended, experimentalists in pollution studies have devised a technique called Differential Absorption and Scattering (DAS), or alternatively Differential Absorption Lidar (DIAL). First proposed by Measures and Pilon (43) and by Byer and Garbuny (44), this technique uses elastic backscattering from atmospheric aerosols, and by gases themselves in place of a fixed retroreflector. A diagram of the DAS technique is shown in Figure 5.8. The elastic scattering cross sections for particles (Mie Scattering) and for molecules (Rayleigh Scattering) are high enough that a detectable, reflected signal can be achieved over kilometer and longer ranges. Moreover, since the "reflector" is extended in space, by appropriate time-gating a mapping of a concentration of pollutants can be made. A

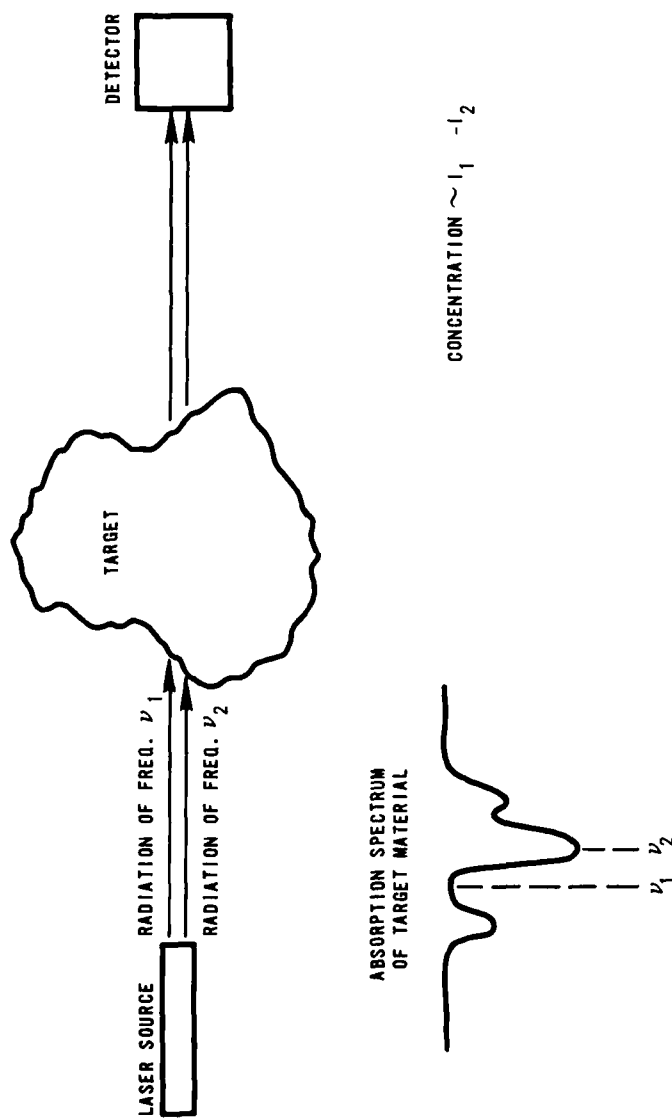


Fig. 5.7 - Scheme for Differential Absorption

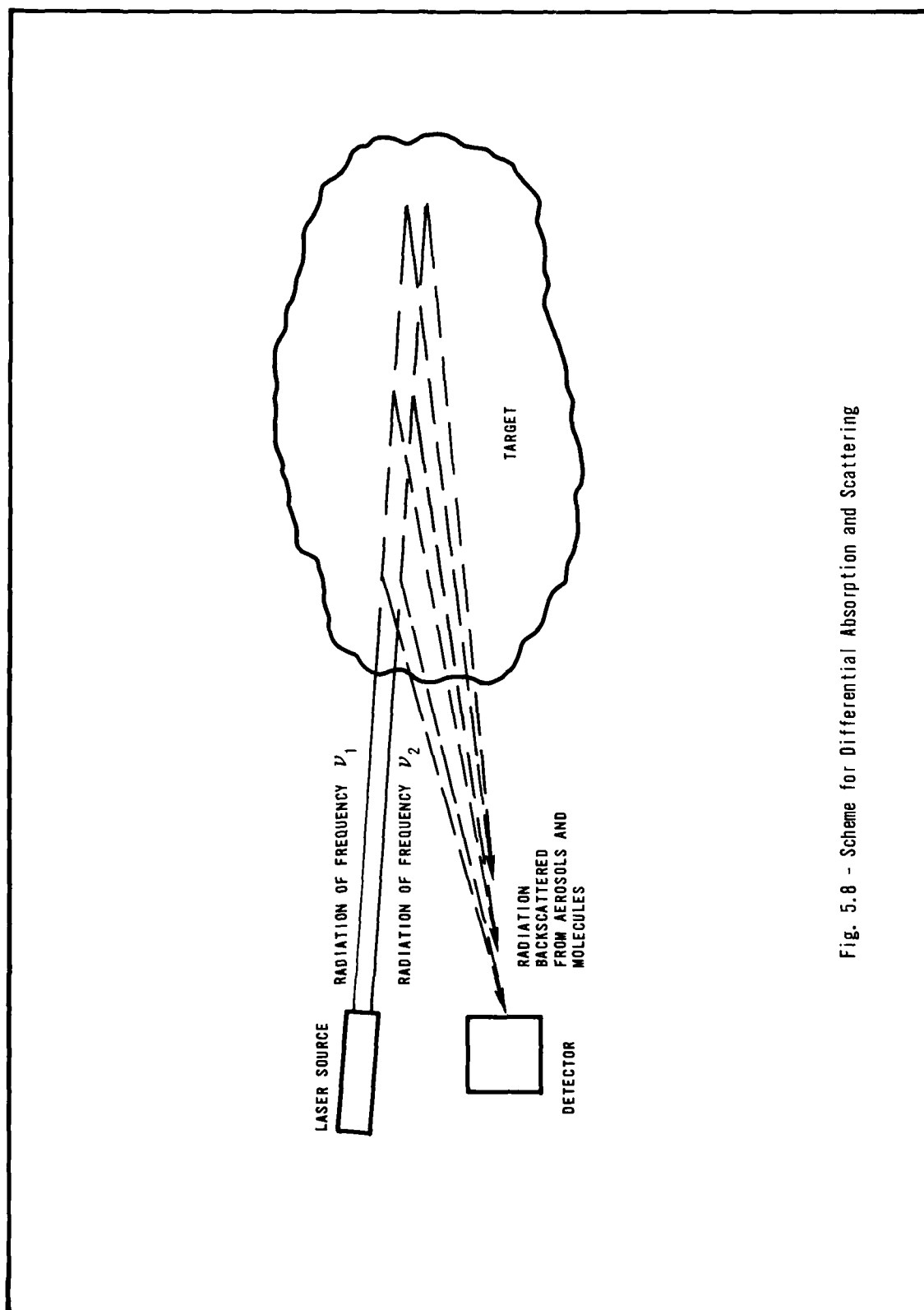


Fig. 5.8 - Scheme for Differential Absorption and Scattering

comprehensive discussion of DAS and its applications is given by Collis and Russell in Laser Monitoring of the Atmosphere (45, pp. 71-151).

In applications of this technique, the emphasis has been on the ability to make measurements of very low concentrations of pollutants over long distances. For example, Rothe, et al, were able to measure concentrations of 0.2 ppm of NO₂ at distances up to 4 km (46). This method depends on the predetermination of the species that are to be detected or measured, and on an accurate foreknowledge of absorption spectra. This requirement is, in fact, the principal drawback of this technique when considered for the detection of hazardous materials.

One can think of adapting the Differential Absorption and Scattering technique to more than one material by using two or more pairs of discrete wavelengths. As a limiting case, a continuous spectrum of incident radiation over a certain interval can be considered. Here, we are back to a situation similar to that discussed in Section 5.2.1.1, Direct Absorption, but with the possibility of atmospheric backscatter instead of a fixed retroreflector. The main considerations in the feasibility of a hypothetical system such as this would be the detectability of the signal, and the frequency range of the source. Assuming that a detection system could be devised with sufficient sensitivity, the principal problem would be lasers tunable over a sufficiently wide range. The dye laser used by Fujii and Masamura in their study of multicomponent mixtures covered 5600 to 6100 Å (0.56 to 0.61 μm) (Reference 47), and the CO₂ laser used in the ILAMS System covers a range of 9-11 μm (48). Diode lasers are tunable over relatively wide ranges, but often in discrete intervals, each of which may be on the order of 1 cm⁻¹ wide (small fractions of a micron at micron wavelengths). The widest tunable range reported for diode lasers employed in atmospheric studies is the lead-salt diode laser used by J. Reid, et al, reported as having a range of 1050 to 1150 cm⁻¹ (49). In addition, tunable diode lasers are relatively low in power (on the order of 10⁻³ W continuous, or 10 W pulsed), and have thus far been used only with fixed

retroreflectors. Thus, the existence of a broadly tunable source of sufficient power is the major impediment to a single-ended scheme adaptable to a wide range of materials which would use atmospheric backscatter.

The Remote Sensing Group at the Edgewood Facility, Aberdeen Proving Ground, is engaged in experimental studies of multicomponent analysis with tunable lasers using both atmospheric scatter and terrain backgrounds (50), and their work should be monitored for applications to hazardous material detection. This effort, however, is presently in only the exploratory stages of development, and moreover, is aimed at the detection of a relatively small group of heavy, asymmetric molecules.

5.2.1.3 Laser Raman Scattering

A single-ended remote technique which has received considerable attention for pollution studies and chemical war agent detection is Laser Raman Scattering. This technique, in addition to being single-ended, has the advantage of using a single frequency source for the detection of many materials. A significant drawback, however, has been the very low cross-sections for Raman scattering processes.

In Raman scattering, a beam of photons of a given energy undergoes inelastic scattering such that the scattered photons exist at energies (frequencies) which are slightly higher or slightly lower than the energy of the incident beam. (The lower frequencies are referred to as Stokes lines, and the higher frequencies as anti-Stokes lines). The energy shifts correspond to discrete states characteristic of quantum vibrational and rotational levels in the molecule. Thus, the set of possible energy levels is unique for each molecule. (The positions of the shifted lines, but not their intensities, are identical to the vibrational and rotational levels observed in infrared spectra.) Raman scattering is generally thought of as an instantaneous process. That is, the incident radiation raises the molecule to a virtual level from which it immediately decays ($<10^{-14}$ sec),

with emission of radiation at a different wavelength. This time regime may be contrasted to that for the fluorescence process, where the excited states decay exponentially with half-lives ranging from 1 μ sec to 1 sec. Raman scattering takes place in all directions around the target material, and in a laboratory a detector is often placed to measure radiation scattered at right angles to the incident beam. For remote detection, however, to keep a system single-ended, radiation backscattered along the same line as the incident beam is detected, even though its intensity may not be as great as that scattered at other angles. A diagram of a Raman detection scheme is shown in Figure 5.9.

Several aspects of the Raman scattering process bear significantly on the possibility of its being used in a practical hazardous material detection system. The relatively low cross sections for Raman scattering have been mentioned. Figure 5.10 indicates schematically the orders of magnitude of cross sections for various optical interaction processes discussed in this section (the resonant Raman and fluorescence processes are discussed subsequently). As can be seen, Raman scattering cross sections are some five or more orders of magnitude lower than absorption and molecular fluorescence cross sections, about two orders of magnitude lower than Rayleigh cross sections, and many orders of magnitude lower than Mie scattering cross sections.

Figure 5.10 oversimplifies, since the various optical interaction cross sections are not constants, independent of frequency. The cross section for Raman scattering varies as the fourth power of frequency (or inversely with the fourth power of wavelength), thus favoring operation in the visible or higher frequency ranges rather than in the IR ranges (in which many of the absorption techniques operate). In reality, there are competing effects influencing the decision of what wavelength to use for Raman experiments. The variation of cross-section favors high frequencies; but frequencies toward the violet and ultra-violet end of the spectrum are high enough in energy to excite fluorescence in most materials. As discussed later, the

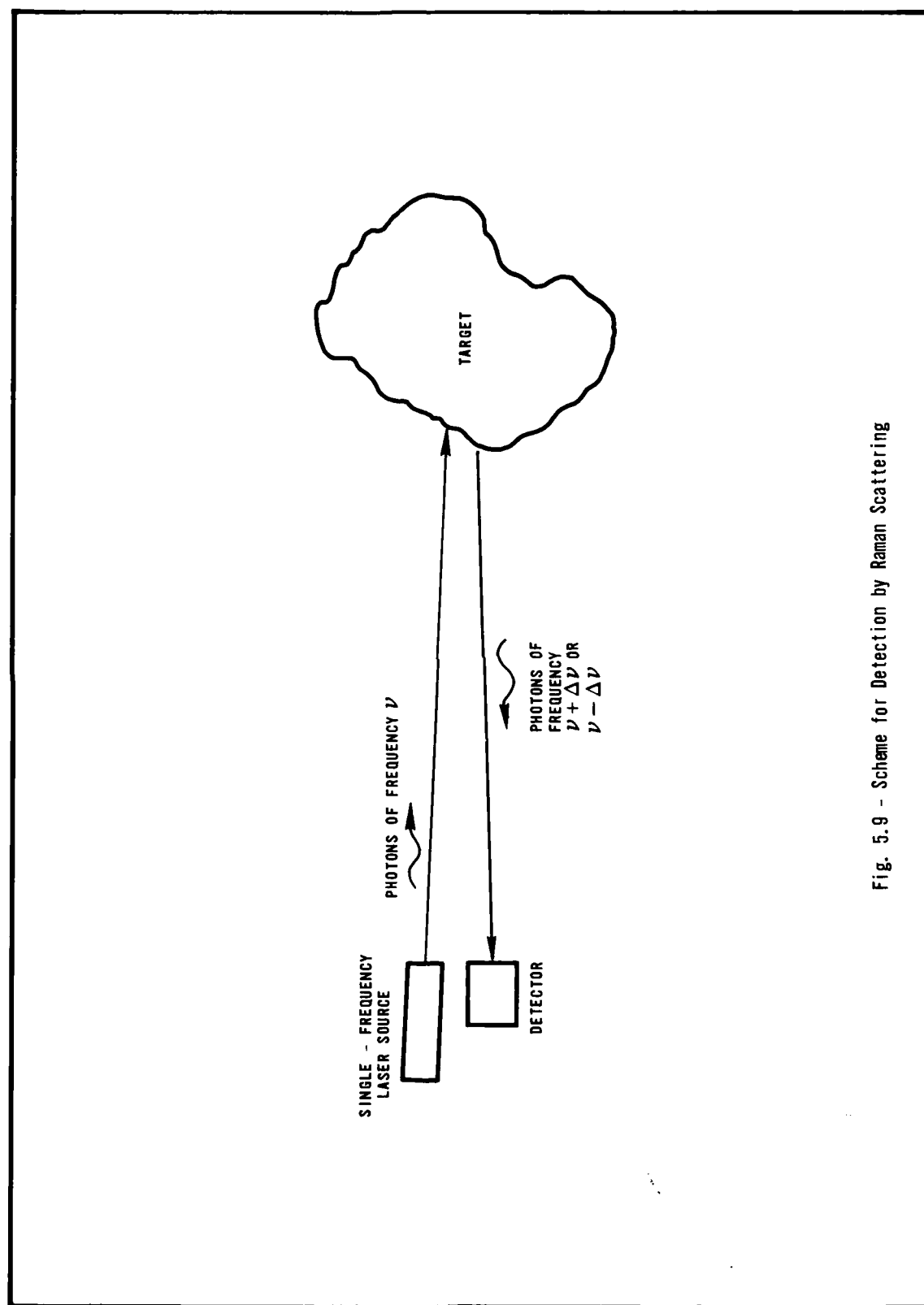


Fig. 5.9 - Scheme for Detection by Raman Scattering

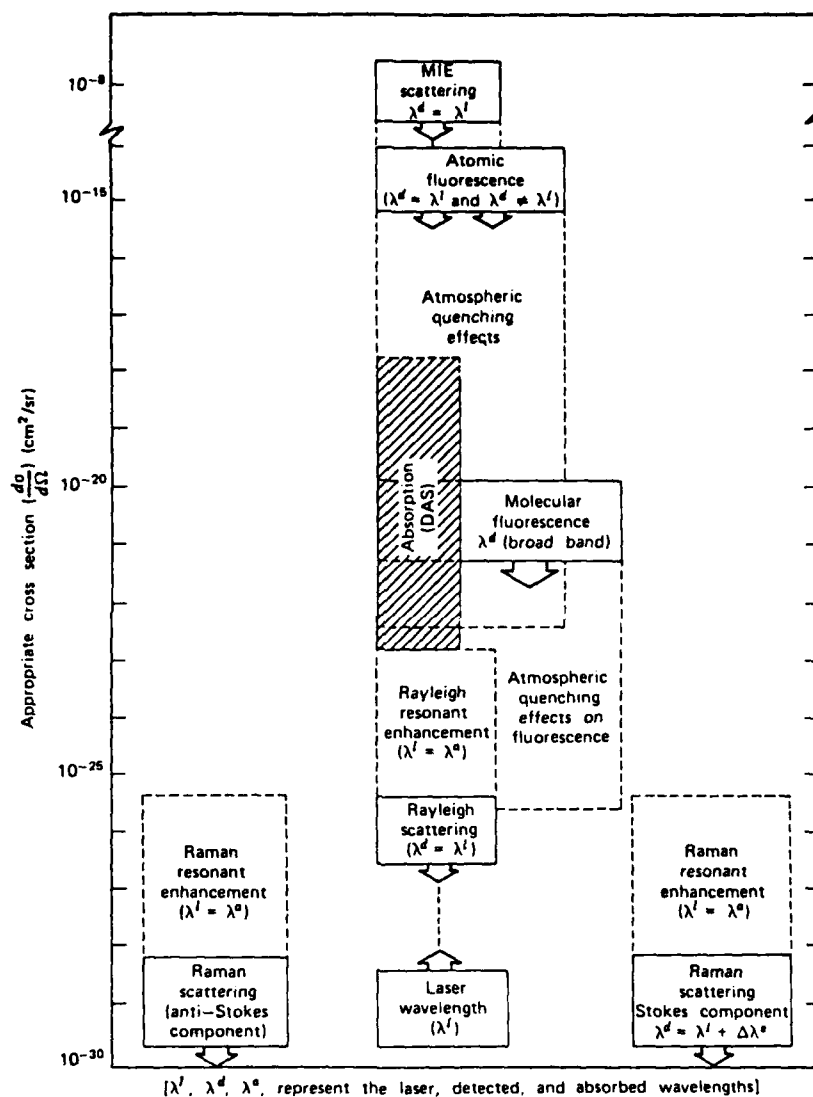


Fig. 5.10 - Relative Cross Sections of Optical Interaction Processes Relevant to Laser Environmental Sensing, Reference 34, p. 300, Used with permission.

fluorescence signals tend to be relatively broadband, and would obscure the fine structure of the Raman spectrum. In the laboratory, Raman experiments are often run in the green, blue, or violet regions of the visible spectrum.

The choice of frequencies suitable for a laboratory experiment can pose serious problems when thought of in terms of a field instrument. Here, eye hazard problems take on greater significance. The cross-sections for Raman scattering would require, even at relatively short ranges, intense laser sources capable of damaging the retina of an eye. Whereas, even in the field, a trained crew of technicians might operate a potentially damaging laser beam safely, the prospect of manufacturing such a laser instrument for widespread use by many fire and other emergency personnel is another matter. The conditions of use might have to preclude the design of any instrument for an intensity and frequency range where serious eye damage could easily result from unguarded direction of the beam. (Even with care, there would be some accident situations where the effect of the beam on people could not be controlled, e.g., where there were houses or buildings on the opposite side of the target material.) The question of a definition of requirements for eye safety is one which should be addressed in any development of instruments operating with visible radiation. With these cautions and drawbacks in mind, it will be worthwhile to look at two hardware applications of Laser Raman Scattering.

In the area of pollution monitoring, a group under H. Inaba and T. Kobayasi has developed a mobile instrument system using Raman scattering (51, pp. 199-201; 52). This system, mounted in a "small coach" was designed for routine monitoring of stack effluent pollutants from ranges on the order of 200 meters. Another mobile system was developed for the Army by Block Engineering, Inc., under the direction of Thomas Hirshfeld, et al (53). The impetus for development of this system was field detection of chemical agents. However, the possibility of application to pollutants was also recognized as the system was developed.

Table 5.1 lists, for both mobile systems, key details including data on the laser systems, dimensions, and performance capabilities. Figure 5.11 is a schematic of the Army/Block Engineering system.

Table 5.1 - Comparison of Data
on Two Mobile Raman Systems

Laser Type	Nd-YAG	Ruby
Wavelength	532.0 nm	347.2 nm
Peak Energy	15mJ/40pps	2J/2pps
Receiver Dimension	50 cm diam.	90 cm diam.
Vehicle	7.6 m (25 ft) coach*	4.5 m (15 ft) flatbed truck +5.5 m (18 ft) trailer
Detection Capability	1850 ppm SO ₂	300 ppm -m, Kerosene
Range	228 m	200 m

*Dimension estimated from photographs.

Several observations can be made from a comparison of data on the two systems. First, the intensities of the laser beams are very high, necessitating physically large systems, and posing the eye hazard problems discussed earlier. (Calculations for the Army System indicated that the frequency doubled ruby laser could cause eye damage at distances of several km (53a, Appendix L)). The large physical dimensions apply not only to the vehicles, a 25' coach and a flatbed truck plus a trailer, but also to the optical systems. Both systems need large receiving telescopes (50 cm and 90 cm diameters) to obtain sufficient amounts of the weak backscattered signal for detection. As they stand, both systems are a far cry from anything that would be portable. On the other hand, the concentrations of materials detected, though high by air pollution standards, are relatively low compared to what might be encountered in a hazardous materials incident. The fact that no development of the

Army's system has occurred since 1972-73 may be significant. Specifically, the Army has dropped the Raman system from consideration as a tactical military piece of equipment because of its complexity (54).

Most recently, a company named Computer Genetics Corp. has placed in operation two mobile lidar (light detection and ranging) systems capable of making measurements using Raman techniques (55). These systems are mounted in three-quarter-ton vans. Raman measurements have also been made aboard a naval research vessel. In addition to Raman techniques, the overall lidar capability of this system includes measurements by Rayleigh and Mie scattering, fluorescence, and by differential absorption.

To date, the Computer Genetics' mobile systems have not been used specifically for the role of identifying unknown hazardous materials. The systems have been used in the Raman mode to record atmospheric water vapor profiles and temperature profiles in water, to provide time and spatial characteristics of a known LNG plume, and to analyze gas turbine engine exhausts. However, the company is known to be interested in the possibilities of a mobile van using Raman as well as other techniques, dedicated to the detection and analysis of hazardous materials. Such a van, though not widely practical for the immediate-response time period, could have significant applications in the intermediate time frame.

In Appendix B we have made an extrapolation of the applicability of a Raman system to incidents involving hazardous materials. For the system parameters assumed in Appendix B, Table B3 shows that energies on the order of 3 to 20 millijoules per pulse would be required to detect hazardous material concentrations on the order of one part per hundred. As noted in the Appendix, these are significant energy requirements for a portable system; and moreover, such a laser system would pose serious eye hazards at ranges of 30 to 40 meters.

It is our conclusion that a Raman System is far from near-term development as a portable field system, and that the potential eye hazard will remain as a drawback for this, or any system in the hands of other than trained operators, and

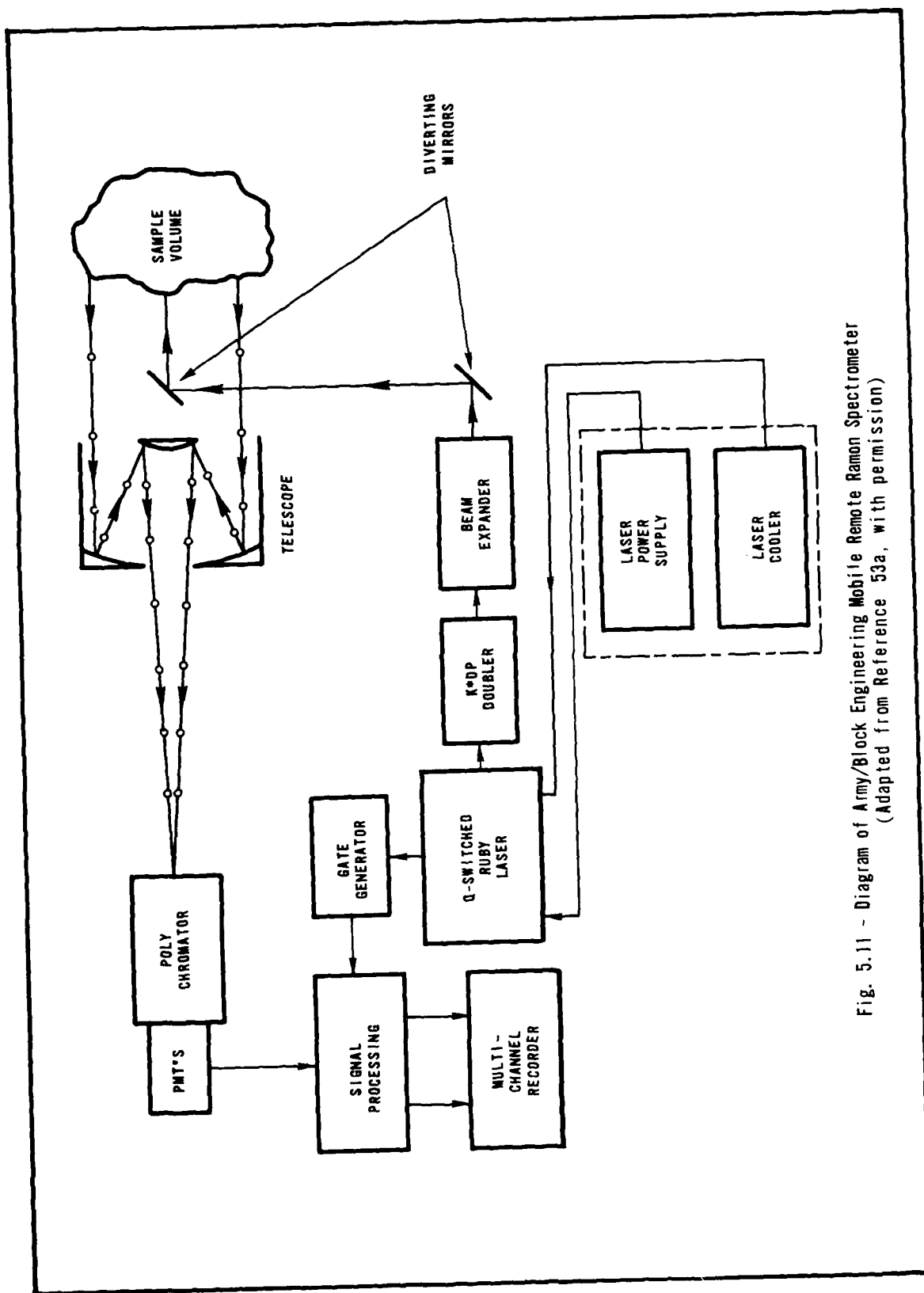


Fig. 5.11 - Diagram of Army/Block Engineering Mobile Remote Ramon Spectrometer
(Adapted from Reference 53a, with permission)

operating in the visible range, no matter what other technical advances are made. However, because of certain features of such a system (its remote, single-ended capability and potential to operate with a single-frequency source), it should not be entirely ruled out in terms of long-range development possibilities.

Several authors have suggested the possibility of taking advantage of what is called the Resonance Raman effect to achieve enhanced Raman scattering cross-sections (51, pp. 129-30; 34, pp. 299-300). As the wavelength of incident radiation approaches the wavelength of an allowed transition in a molecule, the Raman cross-section can increase as much as three orders of magnitude. This advantage is offset to some extent by the difficulty of distinguishing Resonance Raman scattering from fluorescence (a process described in the next section). As noted by Ludwig and Griggs (35, pp. 61-63), the Resonance Raman method appears to have not been developed to any advanced stage of application. Apart from other technical difficulties, the major drawback of Resonance Raman for applications to hazardous material detection is the necessity of foreknowledge of the species to be observed. The wavelength of the incident beam must be selected carefully to match a known spectral line in the target material, a drawback which Resonance Raman shares with Differential Absorption and Scattering. For many materials, a broadly-tunable source would be required, posing the problems already discussed.

5.2.1.4 Fluorescence

The term "fluorescence" is used to describe a process in which radiation corresponding to a specific electronic or vibrational/rotational transition in an atom or molecule is absorbed and subsequently emitted at lower energy. (The term "resonance fluorescence" is sometimes applied to the case where the emitted photon is unchanged in energy; however, "resonance scattering" is the more common term for this process). A sketch

of a fluorescence scheme, if it were to be applied to hazardous material detection, is shown in Figure 5.12.

Though there have been numerous discussions of possible applications of the fluorescence process in remote detection, there appear to have been no developments for routine measurements. Tucker, et al (56), among others, have used fluorescence for in situ measurements of pollution, but their application is one requiring material sampling; that is, it is not remote.

Several characteristics of fluorescent radiation make it less attractive for remote detection than might seem at first glance. For molecules (as distinct from atomic species), the fluorescent signal is spread over a relatively broad spectral range because of rotational and vibrational splitting of the fundamental states. This broadband nature of the signal leads to relatively low signal-to-noise ratios, even though the cross sections for fluorescence are high. Secondly, because the excited states in fluorescence, as distinct from the quasi-instantaneous Raman process, are relatively long-lived, a further reduction of signal intensity occurs. It is possible for a molecule in an excited state to lose energy through collisions with other molecules rather than by the emission of a photon. This degradation is called quenching, a process which can be negligible in low-pressure conditions in a laboratory, but which is significant at atmospheric pressures. Finally, there is the problem common to Resonance Raman and Differential Absorption and Scattering, that the laser wavelength must be matched to a molecule's quantum state(s), requiring a selected wavelength for a single material or a broadly-tunable laser.

5.2.1.5 Heterodyne Techniques

The subject of this section does not represent a new physical process, but rather a detection method which can be applied to several of the processes described in previous sections. This detection method is, however, distinct enough to merit discussion in a separate section.

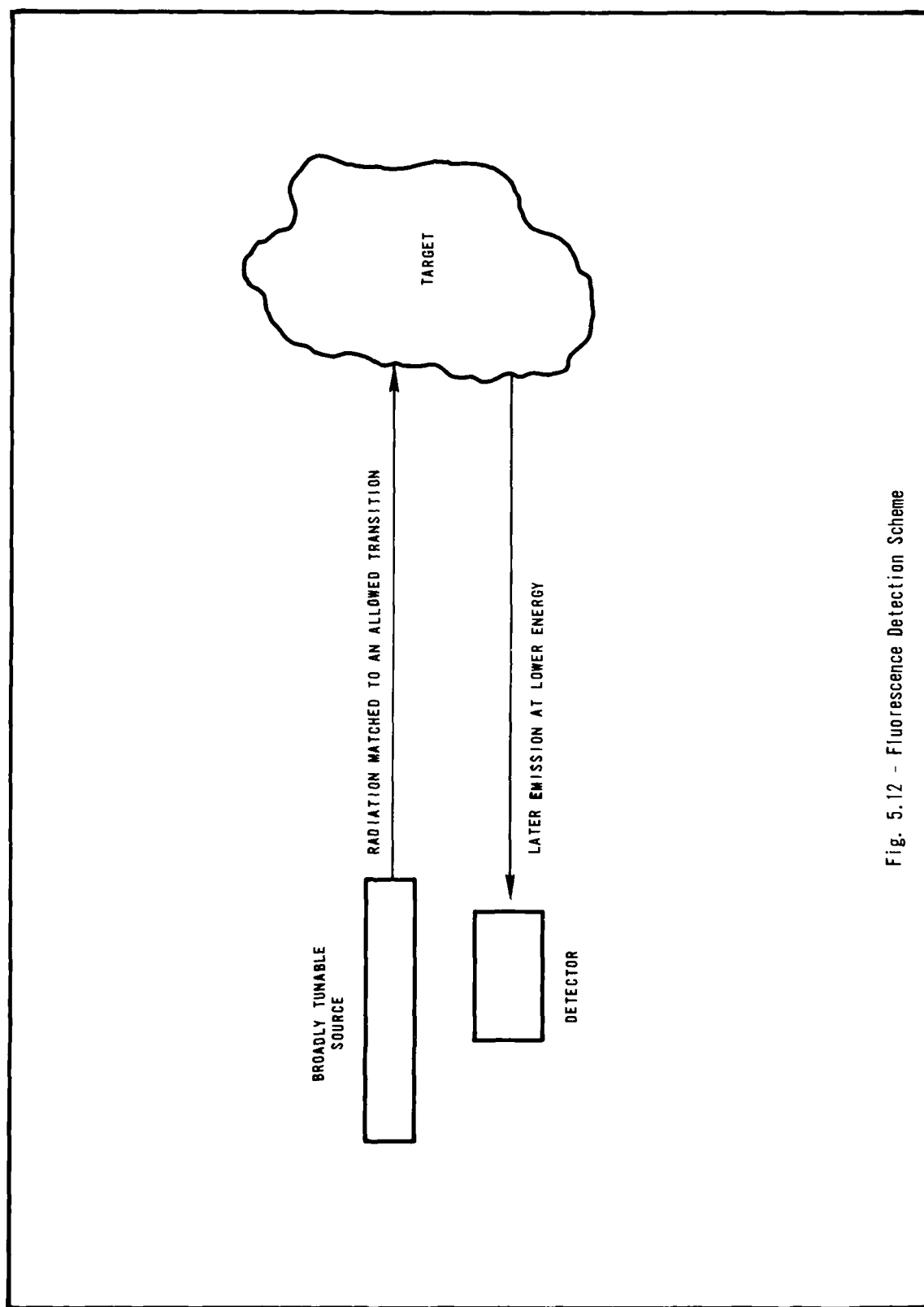


Fig. 5.12 - Fluorescence Detection Scheme

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LOCUS INC STATE COLLEGE PA
INSTRUMENTATION FOR DETECTING HAZARDOUS MATERIALS. (U)
JUN 80 G J GROSS, D E HARRIS, G LACHS

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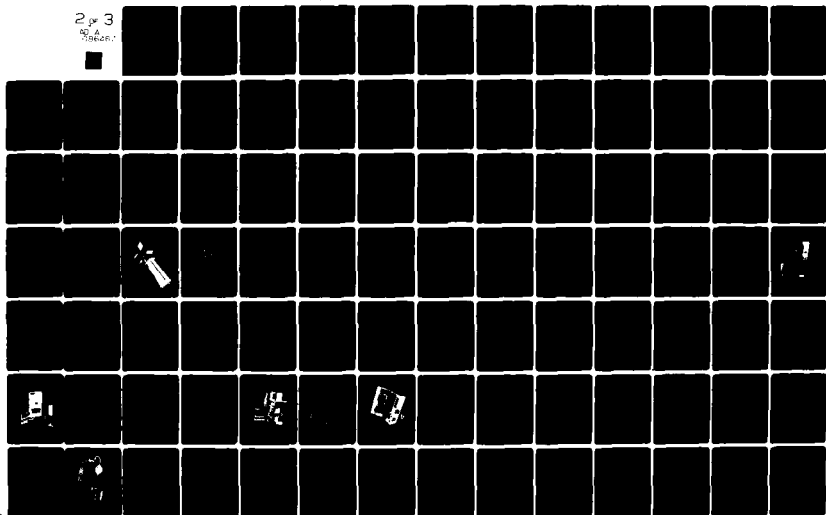
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Basically, heterodyning is used to enhance the detectability of relatively weak signals. In this technique, a laser is used as a local oscillator, and its signal is mixed with the signal from the source to be detected so that the difference frequency, rather than the absolute frequency of the incident radiation, is the quantity of interest. In one application, a tunable laser local oscillator is scanned through the frequency interval of an emission or absorption band of a pollutant. A beat frequency is produced, with the amplitude of the signal related to pollutant concentration.

Heterodyne detection has been applied to differential absorption measurements as in the studies by Menzies and Shumate (42) mentioned in Section 5.2.1.2, and it has been suggested for applications to laser-induced fluorescence measurements (57). It has also been used in a basically passive remote detection scheme to measure atmospheric constituents; for example, ozone, with the sun as a radiation source (58).

As with many other techniques for pollution or atmospheric studies, heterodyne detection has generally been applied to the sensing of a single predetermined substance. The frequency, or frequency range, of the local oscillator must be selected to match closely that of a line or band in the target species. This constraint is, in fact, the major drawback of heterodyne detection for application to the hazardous materials problem. An instrument to detect one out of a large number of possible hazardous materials would need a local oscillator which could be both broadly tunable over a wide range, and also precisely controllable within a narrow frequency range. Such a detection scheme does not seem to be a viable alternative for a portable instrument.

5.2.2 Passive Techniques

5.2.2.1 Passive Infrared Spectroscopy

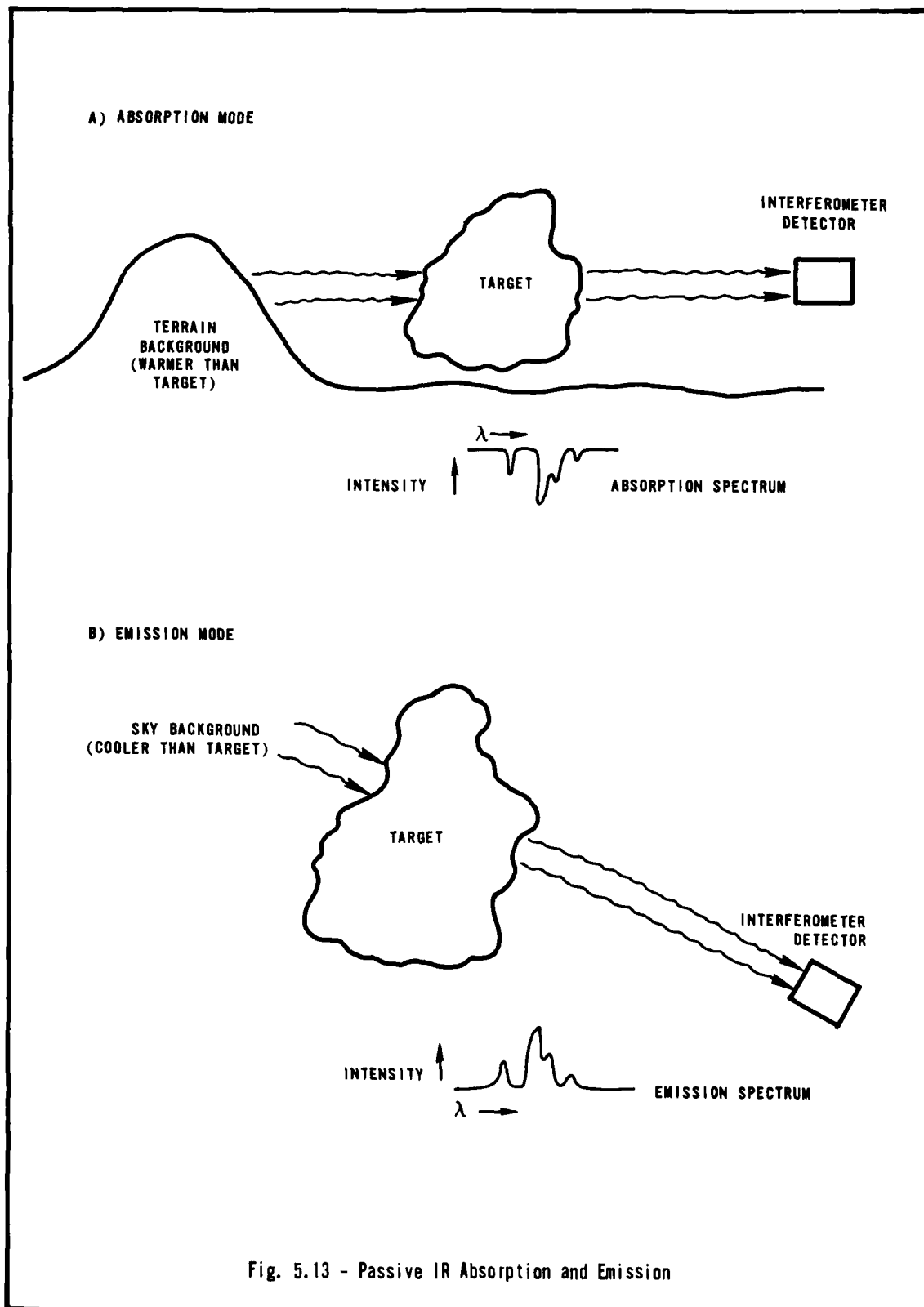
The concept of using natural radiant emissions for the remote detection of gaseous species has been applied by various

researchers in a number of different ways. The warm plume of a smokestack will emit radiation in the infrared characteristic of the species present. Prengle, et al (59), were the first to build a passive remote instrument for the determination of pollutants in gas plumes. With their instrument, an interferometer spectrometer, they made measurements at a distance of 65 meters on plumes at 500-600° K temperatures. The EPA ROSE System, described in Section 5.2.1.1 in its active, double-ended mode, has also been used in a passive mode to view the emissions from warm sources: industrial stacks, waste gas flares, and jet engine plumes.

A group at the Chemical Systems Division, Edgewood Facility, Aberdeen Proving Ground, has sponsored several contracts for the development of instruments to take advantage of small temperature differences between the target material and its background for the detection of chemical warfare agents. The prototype of such an instrument, called the Passive LOPAIR (Long Path Infrared), and a later developmental model, the XM21, are described in further detail in Section 5.4. An instrument of this type does, in fact, represent what is seen as the most promising approach for the remote detection of hazardous materials.

The usual configuration in the remote sensing of a gaseous body in the atmosphere by passive infrared techniques, is to view an opaque object through the gaseous body and the intervening normal air. When the opaque background is at a higher temperature than the gas and the air, the absorption of the blackbody radiation from the background is observed. When the gas is at a higher temperature, the emission of the gas is the observed quantity. Figure 5.13 shows these situations schematically. In order for this system to operate, it is necessary that the background and the gaseous body be at different temperatures. To show this quantitatively, the pertinent expression will be derived.

To simplify the derivation, assume that the air and the gas are uniform slabs with the symbols defined as follows:



Let B_a , B_b , and B_g be the spectral radiances of the air, background, and gas, respectively. The B 's are functions of temperature and frequency as given by Planck's radiation law (60). Also, let T_a , T_b , and T_g be the transmittance of the air, background, and gas, respectively.

The spectral radiance to be measured in the presence of the gas slab (I_g) is given by:

$$I_g = B_a(1-T_a) + T_a B_g(1-T_g) + T_a T_g B_b \quad (5.2.1)$$

where the $(1-T)$ terms represent the emissive strength of that medium (61). The spectral radiance (I_o) as seen by observing the background in the absence of the gas is given by:

$$I_o = T_a B_b + B_a(1-T_a). \quad (5.2.2)$$

In passive infrared measurements, the difference between I_g and I_o is observed. Let:

$$\Delta I = I_g - I_o;$$

then,

$$\Delta I = T_a(1-T_g)(B_g - B_b). \quad (5.2.3)$$

Thus, in order for ΔI to be observed at all, it is necessary that $B_g \neq B_b$. This, in turn, implies that the opaque background and the gas to be measured be at different temperatures. It should also be noted that (ΔI) will be large whenever $(1-T_g)$ is large, and this occurs at the peaks of molecular spectra. The effect of T_a is minimized by utilizing an atmospheric window such as the 8-12 μm band. Another reason measurements are made in the infrared is that, at normal atmospheric

temperatures, the visible portion of blackbody radiation is too small, while the infrared radiation is orders of magnitude stronger.

5.2.2.2 Space Applications of Passive Remote Detection

Because of interest in the composition of both the Earth's upper atmosphere and the atmospheres of other planets, a number of remote sensing techniques have been developed by NASA for use on satellites and spacecraft. From one point of view, the needs or constraints for space-borne instruments are similar to those for portable systems to be used in hazardous material detection. Weight is at a premium for any space vehicle, so light, compact instruments are desirable, as they are for portable ground use. However, there are significant differences between the possibilities for space applications and those for hazardous material emergencies. These differences result in design approaches for space applications which do not favor a direct adaptation of such instruments for emergency use.

One significant difference between space applications and emergency use is that the geometry and layout of the detection scheme can be carefully designed and planned in advance for the space-borne instrument, whereas the emergency user does not generally have this luxury. By geometry and layout is meant, in part, the relationship between a source of radiation, the target, and the detector. For space applications, a relatively high-intensity source of radiation is readily available: the sun. Thus, many instruments for atmospheric studies are passive, using the sun as a source. The space experiment can often be designed or planned in advance so that the spacecraft can have a line-of-sight path through a portion of the atmosphere to the sun, or can view reflected sunlight through the planet's atmosphere.

Figure 5.14 shows a typical configuration for an experiment to study the atmosphere of another planet. For emergency applications, the sun cannot be depended upon as a source for a number of reasons: nighttime clouds, and simple geometry -

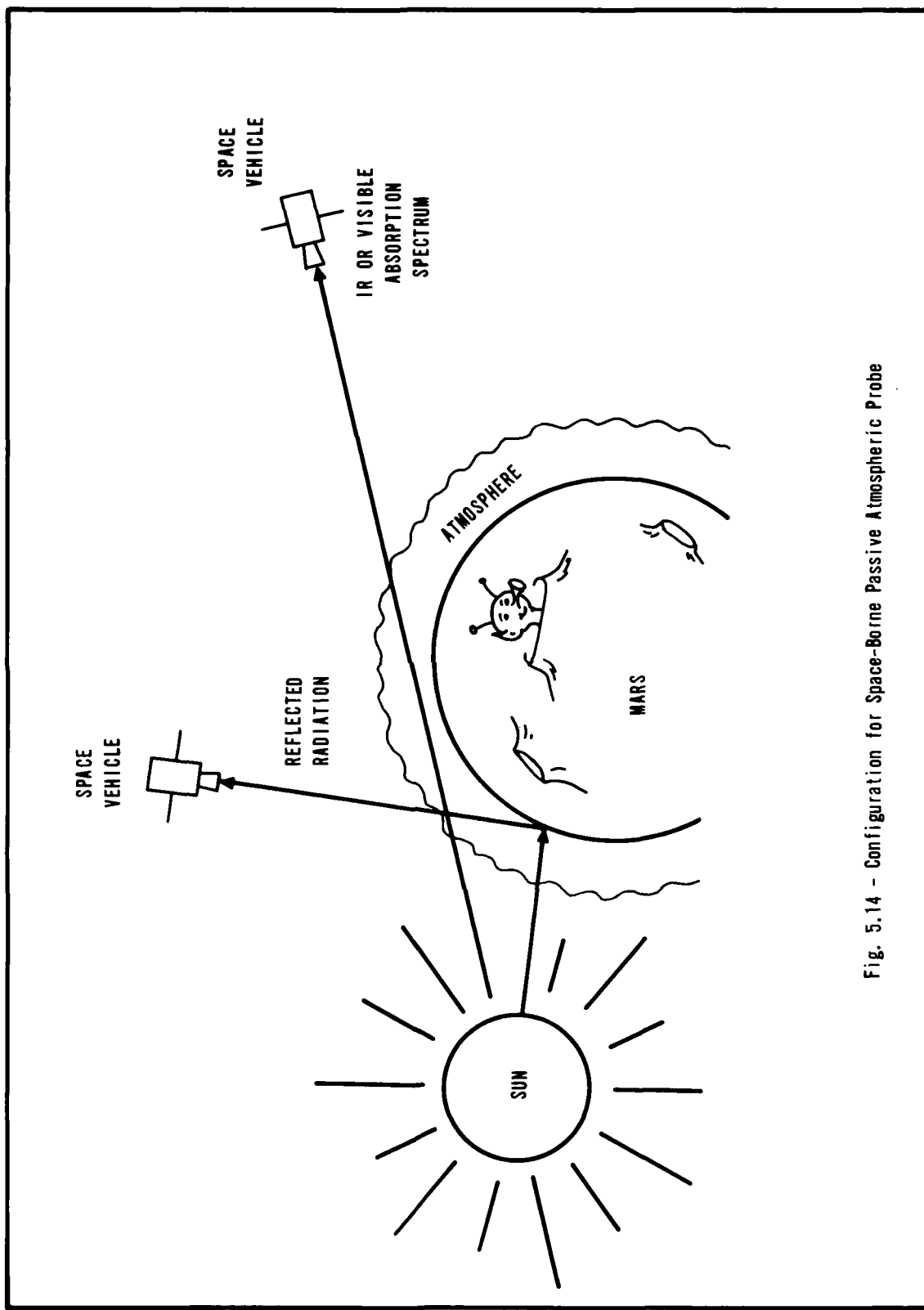


Fig. 5.14 - Configuration for Space-Borne Passive Atmospheric Probe

it might be difficult to get a line-of-sight through a hazardous material vapor cloud to the sun at high noon. The terrain of the planet whose atmosphere is being observed could also be used as a lower temperature source of radiation. From the distance of a satellite, this background would be relatively uniform, whereas, for the close range of hazardous material emergencies, this background would be more heterogeneous with individual buildings, trees, hills, etc., presenting quite different optical or thermal characteristics. This does not rule out the possibility of terrain background as a radiation source for a portable instrument, but does indicate the difference from space applications.

A second difference between space applications and terrestrial (ground-level) use is that the atmospheric density causes a pressure broadening of spectral lines. In the upper atmosphere or higher, one is working in near-vacuum, laboratory-like conditions. Thus, much of the emphasis in space-based experiments is on high-resolution measurements and on the instruments to provide such high resolution. The typical halfwidth of a molecular absorption line is on the order of 0.1 cm^{-1} near ground-level, and 0.001 cm^{-1} in the upper stratosphere (62). An instrument, for example an interferometer, designed to take advantage of this fine structure at high altitudes will simply be too sophisticated for the needs or the possibilities of measurements at standard atmospheric pressures.

Passive instruments have been designed for space applications using heterodyne techniques (63) and a variety of infrared and ultraviolet spectrometers. Table 5.2 summarizes the instrument types flown in a number of important NASA space experiments. The IR spectrometer used in the Skylab experiments (64) was a relatively low resolution instrument with a circular variable interference filter similar to that used in the MIRAN instrument described in Section 6.2.1.2.2. Later instrument applications have stressed increasing sensitivity and better resolution. A few additional words might be said about the High Speed Interferometer (HSI) proposed for the Space Shuttle Program (70). The basic design of this versatile instrument has been used to make pollution measurements in a double-ended mode across the Santa Monica Freeway; to make atmospheric constituent measurements mounted in a down-looking mode on the Goodyear blimp Columbia and collecting reflected sunlight; and

Table 5.2 - Summary of Remote Instruments on Space Missions

MISSION SERIES	OBJECTIVE	INSTRUMENT	REFERENCE
SKYLAB	EARTH RESOURCES	IR FILTER WHEEL SPECTROMETER	64
MARINER	MARS	UV DIFFRACTION GRATING SPECTROMETER	65
		IR SPECTROMETER	65, 66
		IR INTERFEROMETER SPECTROMETER (MARINER 9)	65
VIKING	MARS	IR SPECTROMETER FOR WATER VAPOR DETERMINATION	67
PIONEER	VENUS	UV SPECTROMETER WITH GRATING MONOCHROMATOR	68
VOYAGER	JUPITER, SATURN	UV SPECTROMETER	69
		IR INTERFEROMETER SPECTROMETER	69
SPACE SHUTTLE	EARTH RESOURCES	HIGH SPEED IR INTERFEROMETER SPECTROMETER	70

to measure trace constituents in the lower stratosphere aboard the Anglo-French Concorde, looking at the rising or setting sun. Though planned for eventual space application, this instrument is heavy, with a total weight of 319 pounds (70, p.42). Thus, an instrument of this specific type is not likely to be directly applicable for use as a portable, hazardous material detector.

The passive interferometer systems used in space applications are, in principle, very similar to that to be proposed in Section 5.4. The main differences are a higher resolution (and more delicate) interferometer, and the ability to use telemetry and laboratory-based computers for analysis of data. Thus, the concepts used for spacecraft experiments in remote sensing may be applicable to hazardous material detection, but the specific hardware generally is not.

5.2.2.3 Correlation Spectroscopy

A number of techniques for atmospheric or pollution monitoring have been developed which can be grouped under the heading of correlation spectroscopy. Correlation methods can make use of a sample of the target material, an application discussed in Section 6.0, or they can be remote. One particular remote instrument, the Barringer COSPEC (71), which has been produced commercially and used in the field for a number of years, is briefly evaluated here for its application to hazardous material detection.

The Barringer COSPEC is a dispersive remote sensor which operates in the visible wavelength range, and which is used to measure concentrations of materials from their absorption spectra. The source of radiation for the instrument is light from the zenith sky. In operation, a smoke plume or gas cloud is viewed from underneath, and the skylight passing through it is collected by the instrument. This incoming light beam is dispersed into its spectral components by a grating monochromator and transmitted selectively through a series of masks which have been designed and prepared for the material of interest

(e.g., SO_2 or NO_2). The masks consist of a set with a series of slits corresponding to transmission maxima in the spectrum of the target gas, and a set with slits corresponding to transmission minima. The differences in radiant powers passing through the masks are used to generate the gas signal.

The different objectives between instruments designed for pollution monitoring and those intended for hazardous material detection apply here. The COSPEC is built for use with a known pollutant (the masks are made ahead of time for that substance), and is designed primarily for quantitative measurements.

In principle, there is no reason why a series of masks could not be made for a large number of hazardous materials, and sequentially introduced into the dispersed spectrum to seek a maximum difference signal which would identify the materials. In fact, for a large number of materials, there is no intrinsic reason why a series of physical masks would need to be used. Computerized numerical methods, such as those described in Section 5.4, could be designed to discriminate and identify materials. The characteristics of absorption spectra in the visible range of skylight would, of course, have to be studied in detail. It is likely that a significant enough number of hazardous materials would have distinctive spectral signatures in that range that a workable instrument could be designed and built.

The main drawback of such an instrument is simply that it operates in the visible range, and would only be useful during daylight hours. Such a limitation would seem to be sufficient to rule out development for hazardous material emergency applications. If a use could be shown for an instrument restricted to daytime operation, a system of this type would have attractive potential.

For the sake of completeness, another remote correlation instrument, the JRB Remote SO_2 Monitor (35, pp.77-80), should be mentioned. This instrument collects infrared radiation from a warm stack

plume, and works on the gas filter cell correlation principle. In this technique, incoming radiation is passed alternately along two optical paths, one containing a pre-prepared sample of the gas to be measured, in this case SO_2 . The difference between transmission through a reference cell and through the SO_2 is related to the concentration of the gas. Besides the fact that this instrument depends on the radiance emitted by a warm plume, its requirement of a sample cell of the material to be measured makes its application to a large number of possible materials impractical.

5.2.2.4 Flame Analysis

If an accident occurs, and a vehicle or storage tank is on fire, the possibility of using the flame itself as a source for identifying the material suggests itself. The flame from any material will have characteristic visible and infrared emission lines which could, in principle, be detected by a dispersive instrument.

Flame Emission Spectrometry is used regularly in the laboratory to identify materials or constituents of materials. In these applications, the flame is used as an excitation source for the material to be studied, which is sprayed into the flame. The flame itself, though, has characteristic emissions which could be used to identify the burning fuel. It should be noted that these emissions are due to combustion products which, even in a laboratory situation, are complex, producing complex spectra, depending in part on the conditions of combustion (72, pp. 83-98 and 151-171).

The conditions in an accident are, however, far different from those in a laboratory, and these conditions will more likely than not obscure identifying spectral information from the flame. An open fire, such as would occur in a highway or train accident, tends to have a sheath of unburned or partially burned material about its hot core. Incandescent soot forms a large part of what we see as a visible flame. The typical open

fire appears as a "grey body" with a temperature of about 1200°C (73) (this temperature characteristic of 1200°C is relatively constant for a wide variety of materials engulfed in the flames). Such a fire would provide little identifying spectral information for an observer.

Examination of photographs of fires occurring in hazardous material accidents (74) reveals that there are some fires resulting from leaks in tank cars or trailers in which the flame is relatively clean and unobscured. Spectral analysis of such flames where debris and wreckage do not form a part of the fire should be possible. (Note again though that the conditions of combustion, e.g., whether laminar or turbulent, or whether water vapor is present, strongly affect the nature of spectral emissions (72, pp. 84, 95)). The major question is whether enough instances of this type occur to warrant the development of an instrument applicable only to these special circumstances. The limited usefulness of such an instrument would not seem to justify its development. However, some further analysis of accident statistics and conditions could aid in providing a definitive answer.

The fact that open fires involving different materials tend to have relatively constant temperature characteristics suggests an alternate use of the flame in situations where a fire occurs. One could think of using the flame as a higher temperature source through which to view any unburned gases between the fire and the observer. One would record the absorption spectrum of the unburned gas using an interferometer, monochromator, or an interference filter detection system. There are both technical and practical questions that would have to be answered concerning such a system. The first question is whether an instrument applicable only to fires would be worth developing. The survey data discussed in Section 3 suggests that about 28% of hazardous material accidents might be expected to have accompanying fires. A portable instrument which was developed for a double-ended system, with a lamp as the radiation source, might conceivably be adaptable to looking through

unburned material at the flame as a radiation source. A more difficult technical question is whether open flames could be expected to provide a predictable enough background that they could advantageously be used as a radiation source. The flame conditions in accidents would seem to be variable and complex enough (despite the stated nominal 1200°C characteristic temperature) that experimental studies would have to be performed before the feasibility of such an instrument application could be decided. Such experimental studies could form a concomitant task if a passive IR remote instrument should reach the development stage.

One last way in which the flame from a fire can provide useful identifying information, though not directly, is in the final combustion products in the plume or smoke. A passive IR system, if developed, could be used in the emission mode to observe the warm plume. The discrimination problem in this application is made more difficult by the need to infer, from the combustion products, the identity of the original material. On the other hand, the warm plume will provide a relatively strongly emitting radiation source. The combustion products themselves may in some cases be toxic, whereas the original material was not. In any development of a passive IR instrument, its applicability to analysis of plumes of burning materials should be a major consideration.

Section 5.3 summarizes the advantages and disadvantages of the principal techniques discussed here.

5.3 Summary of Remote Sensing Systems

Descriptions are presented in Section 5.2 of the various remote sensing techniques which have been employed in pollution monitoring and atmospheric constituent measurements. A tabulation of these techniques is presented in Table 5.3 along with a brief description of the salient properties of these systems.

Most of the Table headings are self-explanatory, but some discussion of the column heading "single or multiple species" may be in order. All of the entries in this column marked

Table 5.3 - Summary of Remote Systems

TYPE OF SYSTEM	REFERENCE SUBSECTION	ACTIVE OR PASSIVE	TYPE OF SOURCE	SINGLE OR DOUBLE ENDED	TYPICAL SENSITIVITY IN PPM	SINGLE OR MULTIPLE SPECIES
DIRECT ABSORPTION	5.2.1.1	ACTIVE	LAMP OR TUNABLE LASER	DOUBLE	0.01	MULTIPLE
DIFFERENTIAL ABSORPTION AND SCATTERING	5.2.1.2	ACTIVE	LASER	EITHER	0.2	SINGLE
RAMAN SCATTERING	5.2.1.3	ACTIVE	LASER	EITHER	10	MULTIPLE
RESONANCE FLUORESCENCE	5.2.1.4	ACTIVE	LASER	SINGLE	1	SINGLE
HETERODYNE	5.2.1.5	EITHER	LASER WHEN ACTIVE	EITHER	.002	SINGLE
PASSIVE INFRA-RED	5.2.2.1	PASSIVE	—	SINGLE	0.1	MULTIPLE
SPACE APPLICATIONS PASSIVE SYSTEMS	5.2.2.2	PASSIVE	—	SINGLE	0.2	MULTIPLE
CORRELATION SPECTROSCOPY	5.2.2.3	PASSIVE	—	SINGLE	10	SINGLE
FLAME ANALYSIS	5.2.2.4	PASSIVE	—	SINGLE	—	MULTIPLE

"single" can be used to detect various species of molecules, but they can only examine one species at a time. In order to alter the species of molecule being observed, it is necessary to change the laser frequency (change lasers in many cases) in the differential absorption, resonance fluorescence, and heterodyne systems. In the correlation spectroscopy system it is necessary to change gas cells or spectrum masks when varying molecular species.

Several other comments on the Table should be made here. The heterodyne detection system is listed as either in the "active" or "passive" column of the Table. The primary purpose of the heterodyne system is to utilize the preamplification that takes place in optical heterodyning with a strong local laser (75). This detection system can be employed for observing naturally-stimulated spectra; in such a use the system is passive in spite of the presence of a laser in the receiver because the laser signal is confined to the receiver. Also, the differential absorption and scattering system and Raman scattering system can be operated in either the single-ended or double-ended modes of operation. When these systems are operated in the single-ended mode, they are often used in the manner of pulsed radar, and are called LIDAR systems. These systems can be employed to determine the shape and density profile of a cloud or mist of the species of gaseous molecule being observed.

If a remote sensing system is to be employed for detecting hazardous materials, it must be able to distinguish which of a large list of possibilities (i.e., Table 4.1) is present. This eliminates from consideration as a hazardous material detection system all those systems in Table 5.1 which can only be utilized for one species at a time. It would also be prudent to eliminate from consideration active systems which employ laser sources operating in the visible range. Although such systems can be operated safely by properly trained personnel, the use of lasers in the environment involved in hazardous material

observations, which often includes emergency situations and system operation by firemen, would present too great a safety hazard.

A system which should be useful for hazardous material detection is described in Section 5.4. This system is a combination of the passive infrared technique and a lamp-source excited version of the direct absorption technique. It may be operated either as a passive single-ended system or as an active double-ended system. Advantages and disadvantages of both of these options are described in Section 5.4.

In general, the remote sensing systems listed in Table 5.1 have been applied to obtaining substance densities for low-level concentrations of constituents of the atmosphere. Even those systems which can observe multiple species of atmospheric constituents have monitored only a handful of predetermined species at a time. This differs considerably from the hazardous material situation where there is a very large list of potential species, yet whose concentration levels will be higher than most of the atmospheric pollutants, etc. The higher density usually present in a hazardous material episode is an advantage, while the large list of potential contaminants is a disadvantage. The system described in the following section will utilize many of the component and system developments from atmospheric research, and an attempt will be made to show how some of the more difficult problems posed by hazardous material detection can be met.

5.4 Suggestions for the Design of a Remote Sensing System for Hazardous Materials

5.4.1 Introduction

A list of those hazardous materials which are most likely to be encountered is given in Table 4.1. This list contains more than one hundred substances which are frequently shipped in bulk quantities within the United States. The design of a suitable Remote Sensing System for Hazardous Materials (RSSHM) must be

such that it can identify which, if any, specific hazardous material is present; and, in addition, the RSSHM should be able to yield an approximate estimate of the concentration of hazardous material. The system should be portable, rugged, and durable. It may sit idle for years, and its operation should be simple enough for a fireman to utilize the equipment. These requirements set apart the hazardous material detection problem from the problem of measuring the constituents of the atmosphere. The latter problem (described in Section 5.2) requires accurate information about a small list of substances, and the remote sensing equipment for atmospheric studies has been operated exclusively by highly-skilled research scientists.

The U.S. Army has been developing a remote sensing system called the XM21 for the detection of nerve gases (Project SKY WATCH).^{*} This system is being designed for use by an operator of limited training (a soldier) and must be portable and rugged. The design weight of the instrument is 45 lb. maximum, and it must pass a number of shock and environmental tests. Other specifications are contained in the Statement of Work for the XM21 (76). The XM21 is to be applied to the detection and measurement of much more complex molecules than are observed in the atmospheric remote sensing systems described in Section 5.2. The RSSHM described in this section is a modified version of the XM21 system, and many of the critical components are being developed under the "SKY WATCH" program. A relatively brief description of the unclassified aspects of a modified version of the XM21 system is given in Section 5.4.2.

An important aspect of the XM21 is the manner in which it processes the output from the detector with a decision algorithm implemented by a special-purpose computer. The decision algorithm, however, is based upon searching for the potential presence

^{*}A preliminary version of this system called LOPAIR is described in the open literature (see Reference 37). The information about the present state of the unclassified aspects of the project was obtained in a private meeting with D. Flanigan (Project Director) on November 13, 1979.

of a small number of substances and, as such, it may not be suitable for the RSSHM. An alternative algorithm for processing the detector output is described in Section 5.4.3. This alternative system (77) was developed for utilization in gas chromatography, but it is felt that it can be adapted to the RSSHM.

The XM21 system is designed to observe spectra in the 8-12 μm portion of the spectrum. This band coincides with an atmospheric window, and, as discussed in Section 4.4.2, most of the substances listed in Table 4.1 have significant spectral components in that spectral range. Unfortunately, not all of the hazardous substances in this list have spectral components in this band, and alternatives for coping with such substances are discussed in Section 5.4.4.

The basic parts from which the overall system would be built are described in Sections 5.4.2 through 5.4.4. In Section 5.4.5, those aspects of the system discussed previously are summarized, and a possible design for an RSSHM is proposed. In the Conclusion, Section 8.0, some suggestions are made for proceeding with the development of the RSSHM.

5.4.2 Modified Version of the XM21 System

5.4.2.1 Overview

The basic building block for the system is a slightly modified version of the XM21 system mentioned previously. A schematic diagram of the proposed system is shown in Figures 5.15a and 5.15b.

The XM21 system is a passive infrared system which views an opaque object through a combination of normal air and the gas to be measured. A general description of such systems was given in Section 5.2.2.1. Equation 5.2.3 of that section shows that the strength of the difference signal (ΔI) is proportional to the difference between the spectral radiance of the background and the spectral radiance of the gas. This difference in spectral radiances of the blackbody sources is a

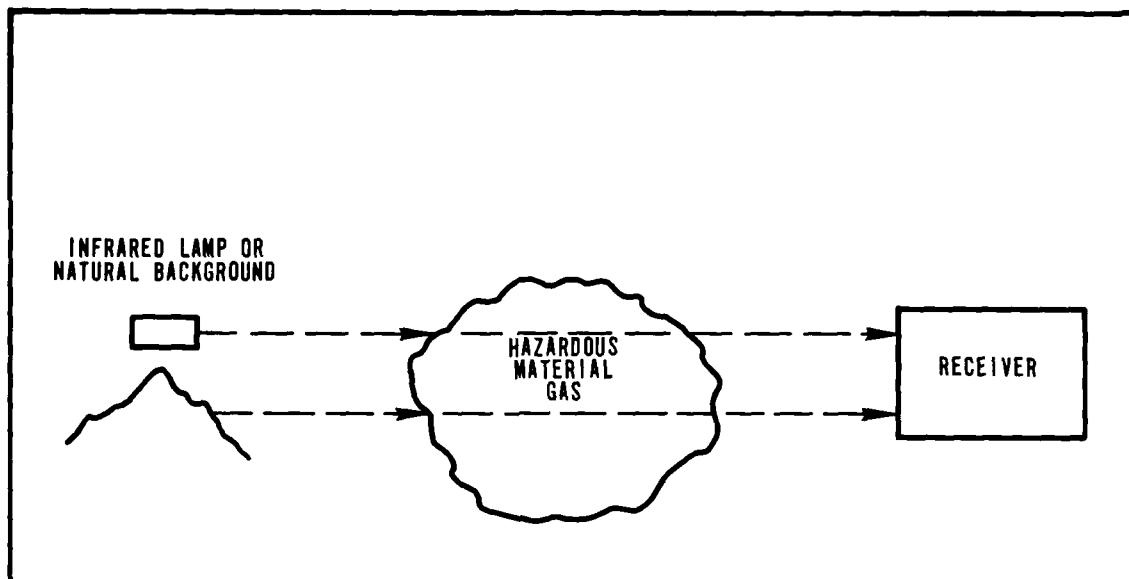


Fig. 5.15a - Geometry of the System

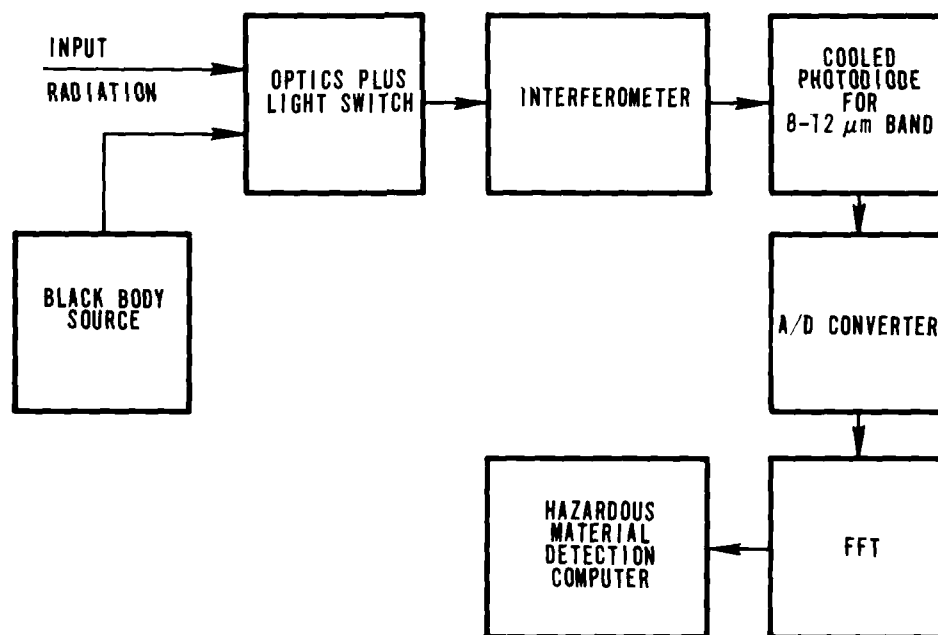


Fig. 5.15b - Block Diagram of the System

Fig. 5.15 - Schematic of Proposed Instrument System

monotonically (non-linear) increasing function of the temperature difference between the gas and the opaque background source. There are obvious advantages in the utilization of a passive system in a battlefield environment, but that same advantage does not necessarily apply in the hazardous material detection system. In particular, the opaque background source could be replaced by an infrared lamp, and thereby greatly increase the above-mentioned temperature difference. This implies the use of a double-ended system instead of the single-ended system which would exist in the passive application. However, the utilization of an infrared lamp would lead to a much stronger signal, plus an important simplification in the receiver which is discussed in the next subsection. Consideration of a double-ended system does not rule out the possibility of employing a single-ended passive system, and both types should be investigated.

5.4.2.2 Receiver

A block diagram of the receiver for the basic system is shown in Figure 5.15b. Note that it is very similar to the general interferometer receiver system shown in Figure 5.1b. The difference is the addition of a blackbody source at the input to the receiver, and the inclusion of a hazardous material decision computer. The temperature of the blackbody source is set equal to the ambient temperature of the gas, which is assumed to be the same as the ambient temperature of the air.* The purpose of this calibrated blackbody source in the receiver is to provide an infrared source to generate the difference signal described in Section 5.2.2.1. The difference signal is generated by alternately observing the gaseous body to be measured, and the calibrated blackbody of the receiver. It may be possible (some experimentation would be required) to eliminate this somewhat clumsy aspect of the receiver by utilizing a sufficiently bright infrared lamp as the active source shown in Figure 5.15a. This would cause the spectral radiance of the infrared lamp to be

*This may not always be a valid assumption for hazardous materials.

much stronger than the spectral radiance of the gas, and thereby remove the necessity for the blackbody in the receiver. This simplification would only come about if a double-ended system were utilized.

A ruggedized version of the interferometer called a "flex pivot interferometer cube" has been developed by the Air Force Cambridge Laboratories under the direction of John Rex (78), and has been extensively proven in many flights aboard NKC-135 aircraft. A version of this interferometer is being adapted for use in the SKY WATCH Program. It is assumed that some version of this device will be available for use in the hazardous material detection system.

The basic system described in this section is to respond to infrared light in the 8 to 12 μm band. All semiconductor diode detectors which operate in this portion of the spectrum (Hg:Cd:Te, for example) must be cooled to liquid nitrogen temperatures (77°K). A closed-cycle cooling system can be utilized to supply the required cooling without external liquid nitrogen (or any other external coolant). In particular, a very compact closed-cycle cooling system called a "split-cycle Stirling cryogenic cooler" has been developed by the Martin-Marietta Corporation for the Army under Contract No. DAAB07-77-C-0631 (79). This cooler is to be used in the XM21 system and should be able to perform the cooling required for the infrared detector in the RSSHM quite adequately.

This "flex pivot interferometer cube" and the "split cycle Stirling cooler" are important developments which are essential to permitting the hazardous material detection system to be both portable and rugged. The hazardous material decision computer and the Fast Fourier Transform parts of the receiver (if this option is chosen) will be constructed from integrated circuit chip microcomputer elements. These will be rugged, light, and consume relatively small amounts of power. The operator of the system will not be required to do any computer programming, so the pertinent computations have to be built into the system.

The computer design will depend on the detection and decision algorithm to be utilized. In subsection 5.4.2.3, the algorithm which is to be used in the XM21 system is described, and an alternative algorithm is presented in Section 5.4.3.

5.4.2.3 Decision Algorithm of the Basic System

The decision algorithm described here is essentially the same as that of the original LOPAIR System (37). The capability of that system was demonstrated by a measurement of the concentration of dimethylmethylphosphonate in the air. The LOPAIR System provided a test of the overall concept to be utilized in the XM21 System.

The basic measured quantity before the decision computer processing begins is the 8-12 μm spectrum of the incident radiation. The original LOPAIR System utilized a circular variable filter (80) based spectrum analyzer, but the new system will utilize an interferometer combined with a Fast Fourier Transform (FFT) computer to obtain the desired spectrum. The interferometer output, which is the autocorrelation function of the incoming light, is sampled at about 100 equal intervals.* These 100 sample points are digitized and utilized to compute, via FFT, 100 equally-spaced values of the spectrum. This means that the output of the FFT computer leads to a spectrum evaluated at 100 equally-spaced points in the frequency domain of the spectral range 8-12 μm (25-37.5 Terahertz). The spectrum is then mathematically treated as a 100-component vector.

The situation examined by the original LOPAIR System will now be considered. This system searched for a single "target" gas whose spectrum in 100-component vector form is denoted by \bar{f}_t . The constituents of air, including dust, also produce spectra in the 8-12 μm region, and those spectra are denoted by \bar{f}_j . It can be shown (81) that there exists a weighting vector \bar{W} with the property that:

*128 equal intervals would be more convenient for FFT, but 100 was quoted at the private meeting with D. Flanigan on November 13, 1979.

$$\bar{W} \cdot \bar{f}_t = R > 0 \quad (5.4.1)$$

$$\text{while, } \bar{W} \cdot \bar{f}_j = 0 \quad (5.4.2)$$

for all the interferent spectra due to atmospheric constituents other than the target substance. It should be pointed out here that different concentrations of atmospheric substances such as dust must be treated in this system as separate spectra, \bar{f}_j . The determination of a normalized weighting vector which satisfies Equation 5.4.2, while at the same time maximizing R in Equation 5.4.1, is a well-known problem in linear programming (82). The weighting vector, \bar{W} , is found by utilizing well-known computation techniques for the Simplex Method of solution (83), a method often used for pattern recognition problems. The actual running time for computing \bar{W} may be significant even on a large computer. However, once \bar{W} is found for a particular target substance and interferent spectra, it is not necessary to compute it again. Once \bar{W} has been found at some computation center, the numerical values for the components can be incorporated into Read Only Memory (ROM) type devices, and these ROMs can be built into the receiver. The remote sensing system in the field does not compute \bar{W} , but rather uses the \bar{W} stored in the non-volatile part of its computer memory.

The \bar{W} obtained for a particular target substance will only be useful if that particular target (as well as dust and air) is present. If an unexpected substance is present, the system may not operate properly. One can obtain an operational system if only one hazardous substance is present at a time by using the following procedure:

- 1) Find a separate optimum weighting vector \bar{W}_h for each HM entry in Table 4 as though that particular HM were the only one present in the air.
- 2) Incorporate each of these vectors \bar{W}_h and the spectrum of each material \bar{f}_h by storing the pertinent components on ROMs.

- 3) Let \bar{f}_r be the received spectrum. Compute $R_h = \bar{w}_h \cdot \bar{f}_r$ for each hazardous material, and select the material corresponding to the largest R_h as the hazardous material present.
- 4) The value of R_h is proportional to the concentration length and, if the absorption cross-section is known, the concentration can be found. If the maximum R_h is less than some predetermined threshold value, it assumed that none of the HM being tested is present.

The above algorithm may need to be modified to incorporate the effect of some parameters such as the absorption cross-section, and also the fact that the target spectra are affected by the temperature and the density of the surrounding constituents. It also may be possible to find weighting vectors for several substances at a time and thereby simplify the receiver somewhat. Nevertheless, the preceding algorithm presents at least one method of satisfying the RSSHM requirements, and the computer required to accomplish this can be constructed readily with present-day digital technology.

An alternative algorithm which is not as sensitive to the number of hazardous materials present is described in Section 5.4.3.

5.4.2.4 Cost of Basic System

The cost of the first prototype of the XM21 is about \$100,000, and the cost per unit of the first batch (number unknown) will be about \$10,000 - \$20,000.* Eventually, it is hoped that in production volume the cost per unit will be several thousand dollars. Because of the similarity between the RSSHM described here and the XM21 System, upon which it is based, the per-unit cost of the RSSHM should be about the same as the above-

*This cost information is based upon conversations held with D. Flanigan's group at Edgewood Arsenal on November 13, 1979.

mentioned numbers. Some reduction in development cost may be anticipated though, due to the fact that the rugged version of the interferometer and the diode detector cooling system will already have been developed. It may also be possible to utilize the results of the field tests of the XM21 which are to be carried out in 1980, if that information is unclassified.

5.4.3 Alternative Detection Algorithm

5.4.3.1 Introduction

The detection algorithm described herein is based upon the work of G.W. Small, R.T. Rasmussen, and T.L. Isenhour, which was recently described in Applied Spectroscopy (77). Their detection system, which was designed for gas chromatography, can be employed to determine which substances are present out of a large list of possible substances. Their algorithm differs from that described in Section 5.4.2.3 in two fundamental ways. First, they utilize the interferograms directly in their decision process instead of using the spectrum, and thereby remove the need for an FFT computer. Secondly, their decision algorithm, which is based upon vectors, is, nevertheless, different from the previously described decision-algorithm. These aspects will now be discussed in greater detail.

5.4.3.2 Direct Use of Interferograms

Since the interferogram and the spectrum are Fourier Transform pairs, they both contain the same information. By avoiding the FFT calculation, it is possible to simultaneously improve the accuracy of the system and simplify the electronics. One common method to improve the signal-to-noise ratio of the system is to superpose (co-add) several repeated interferogram measurements. A similar process can be employed with the spectrum, but it is not as effective because the power spectrum is non-negative. The interferogram can be negative, and this characteristic improves the noise cancellation incurred in the superposition process. One disadvantage of the interferogram is that it does not show directly where the pertinent spectral

components are as this type of information can only be obtained by taking the Fourier Transform of the interferogram.

In the technique developed by Small, et al (77), only a portion of the total interferogram is actually employed. The entire interferogram is subdivided into 2098 equally-spaced intervals, and the information utilized is from a 100-point segment which begins 60 subdivisions from the light burst. (The light burst is the strong central peak of the interferogram.) The 100-point segment is co-added with the mirror image 100-point segment on the other side of the light burst. These segments were found to contain sufficient information for the successful operation of the detection algorithm. These numbers are included here for the purpose of pointing out that the laboratory system utilized by Small, et al, has greater resolution (2048 points) than the XM21 system (100 points). Thus it would be necessary to verify experimentally whether the algorithm of this section will function satisfactorily with the poorer resolution equipment to be utilized in the portable (outdoor) hazardous material detection system.

5.4.3.3 Decision Algorithm

The 100-point versions of the interferogram described previously are utilized to form 100 component vectors. These vectors are processed differently than the method described in Section 5.4.2. In a hazardous material application, the operator must first take several measurements of the interferograms produced by the air in the absence of the potential hazardous gas to be observed. Several such measurements are made (10 were used by Small, et al.) of various views of the air near the hazardous material gas, but not through it. Each of these is then utilized as a 100-component vector, and an orthonormal set of basis vectors is generated from this set of vectors, using the well-known Gram-Schmidt Orthogonalization Procedure (84). These basis vectors are then subsequently employed to subtract out the effects of the natural components of the air from the vector obtained by observing the hazardous material gas.

Let \bar{X}_k be the 100-component vector obtained from the measurement of the k^{th} clear-air interferogram. Then let B_k be the corresponding orthonormal basis vector such that:

$$\bar{B}_i \cdot \bar{B}_j = \begin{cases} 0 & \text{if } i \neq j \\ 1 & \text{if } i = j \end{cases} \quad (5.4.3)$$

Now let \bar{X}_h be the vector obtained directly from the interferogram of the hazardous material observation, and let \bar{Y}_h be the vector which is obtained after the background (air without the hazardous gas) is subtracted out. That is:

$$\bar{Y}_h = \bar{X}_h - \sum_{k=1}^n \bar{X}_h \cdot \bar{B}_k \bar{B}_k \quad (5.4.4)$$

where n is the number of clear-air samples.

In order to determine which hazardous substance (if any) is present, the following procedure is employed:

- 1) A set of reference interferogram vectors for each gaseous entry in Table 4.1 is prerecorded and stored in the receiver computer memory. These vectors will have been normalized to unit length. Let \bar{R}_j be a typical stored vector.
- 2) Form the dot product $\bar{Y}_h \cdot \bar{R}_j$ for each of the reference vectors.
- 3) The largest dot product will correspond to the gaseous material which is present, and the magnitude of that dot product will be proportional to the concentration length of the hazardous material.

This describes the alternative detection algorithm. There are a few fine points which require explanations too lengthy to include herein. The system has been successfully demonstrated in a laboratory environment, but as yet we know of no attempt to apply this system in an environment such as that required for hazardous materials. The possibility of

using this algorithm in the XM21 System is, however, being considered on that program.*

5.4.4 Materials Not Detectable by Suggested Design

Certain materials are not detectable at all, or are marginally detectable by a passive IR system such as described in the previous sections. Most significant is the group of symmetrical diatomic molecules, including chlorine, which do not emit IR spectra. There are also a few, though not many, materials with no peaks, or very weak peaks, in the 8-12 μm wavelength range. Finally, there are the non-volatile materials, liquids and solids, which do not present a vapor cloud amenable to remote IR detection. The following paragraphs discuss briefly possible ways to cope with these classes of materials.

The easiest situation to deal with is that in which no vapor cloud sufficient for detection is present. If a solid, for example, ammonium nitrate, or a non-volatile liquid is involved in an accident, the absence of a detectable vapor cloud suggests that a close approach by an emergency worker, perhaps wearing protective clothing as a precaution, would be possible. In such an instance, then, the procedure would be to obtain a sample of the material and identify it by one of the non-remote means discussed in Section 6. A detailed examination of the characteristics of reflected or emitted radiation from large pools of liquid or from solids for purposes of identification has been beyond the scope of this study, but such possibilities could be looked into.

For materials whose spectra do not show sufficiently strong peaks in the 8-12 μm range, the possibility exists of working toward extending the wavelength range of the detector in a remote IR instrument. There are, however, physical limitations to what can be achieved in extending the range of detectability. Strong atmospheric absorption bands cover the

*Discussions with D. Flanigan on November 13, 1979.

region from about 5.4 to 7.5 μm and the region above 14 μm , making these wavelengths virtually unavailable where significant amounts of air intervene between the radiation source, target, and instrument. At the wings of the 8-12 μm band, say from 7.5 to 8 and 12 to 14 μm , the problem becomes one of increasing difficulty in resolving the target signal from atmospheric background. For wavelengths below about 5.4 μm , there exist alternate atmospheric absorption bands and windows, making portions of this spectral region available for discrimination. Once a basic instrument is developed, attempts could be made both to increase the useful range of detecting elements and to improve the target-background discrimination capability.

The materials from our selected list which show the greatest problems in this category are acetylene and hydrogen chloride. Acetylene appears to have no resolvable peaks between 8 and 12 μm , but does have a broad band beginning at 12.2 μm and a sharp peak at 3.05 μm . Hydrogen chloride has a weak peak at 9.5 μm - whether strong enough for detection would have to be determined experimentally. It does, however, have a somewhat stronger peak at 14.3 μm and a series of very sharp, strong peaks through the 3.3 to 3.8 μm region. Thus, both of these materials are potentially detectable at wavelengths outside the 8-12 μm region.

The group of symmetrical diatomic molecules presents the most serious problem for any IR system. This group includes chlorine, as already mentioned, as well as the highly-hazardous fluorine and bromine, and the compressed or liquified gases, hydrogen and oxygen. (Oxygen, though not normally thought of as hazardous, is included in the list because of its potential for oxidizing other materials and for creating atmospheres where other materials may more readily burn, or even explode.) Symmetrical diatomic molecules are not "infrared active" since radiation in the infrared region is caused by molecular vibrations and rotations, which in turn produce electric dipole moment changes. Because of charge symmetry, molecules in this

group possess no permanent dipole moment, nor do the possible stretching, bending, or rotational motions produce dipole moment changes (23, pp. 99-102).

Several approaches could be taken to deal with the absence of IR spectra from these molecules. Conceivably, a readout procedure could be devised for a remote IR instrument which would distinguish between a null reading (no spectral peaks other than background), meaning that some species of symmetrical diatomic gas is present, and a reading where spurious peaks are present (peaks not contained in the instrument's recognition library), indicating the presence of some unknown or undeterminable material.

Since the number of symmetrical diatomic materials is small, training of emergency personnel to recognize these materials without instrumentation would be valuable. The chief offenders are chlorine, a greenish-yellow gas; fluorine, a pale yellow gas; and bromine, a reddish-brown fuming liquid. There are not many yellow/green gases or reddish-brown fuming liquids. In an accident where such a material is observed, it would be wise to assume the worst, and take necessary precautions. Moreover, the sense of smell could be brought into play. Chlorine, for example, produces a detectable odor at levels (3.5 ppm) well below those where physical dangers exist. Levels of 15 ppm cause immediate throat irritation, and concentrations of 50 ppm are dangerous for short exposures (15, p. 539). Thus, chlorine (unlike some other toxic gases), by reason of its irritating properties, gives advance warning of dangerous concentrations. Finally, these materials may react with other materials to form secondary products which are infrared active. Again, using chlorine as an example, it reacts with moisture to liberate nascent oxygen and to form hydrochloric acid. (The detection of secondary products is a method that could be considered in general for other materials whose spectra make direct detection difficult.)

Conceivably, some back-up system could be developed for use with a passive IR instrument, to help discriminate materials

that are not infrared-active. The simplest back-up system would consist of a direct sampling technique, for example, "Draeger" tubes (discussed in Section 6). Such tubes exist commercially for chlorine and bromine, and should be able to be developed for fluorine, perhaps with a material other than glass for the case. A back-up remote system, operating in the visible or ultra-violet, might possibly be developed. Detailed consideration of such a system would seem to be premature, since the primary system itself is only at the pre-design stage.

5.4.5 Summary of the Proposed Hazardous Material Sensing System

The proposed remote sensing system for hazardous materials (RSSHM) is based upon a modified version of the XM21* nerve gas detection system. The RSSHM system would measure the 8-12 μm spectrum of the gas being observed, and then employ a well-known algorithm developed for pattern recognition to determine which hazardous material (if any) is present. It would also provide an approximate value for the concentration of the hazardous material. The RSSHM will be portable, rugged, and capable of being operated by a user with limited training. These same requirements apply to the XM21 system, and many of the critical components for the RSSHM have been developed under the XM21 Developmental Program.

The XM21 system upon which our RSSHM design is based is a strictly passive system; hence, it is a single-ended system. It would be advantageous for observing hazardous material if a passive single-ended system would be employed, but this is not the overriding requirement that it is in a military environment. There are some advantages to using an infrared lamp and a double-ended system in terms of signal levels and receiver simplification which are fully described in Section 5.4.2. Some research needs to be performed on the proposed RSSHM to determine if a passive single-ended system will operate satisfactorily.

*See footnote on p. 101.

Block diagrams of the single- or double-ended version of the proposed RSSHM are shown in Figures 5.15a and 5.15b. Thanks to the development program for the XM21, all necessary components exist, and the system will be readily portable. Nevertheless, the XM21 system itself is still in the developmental stage, and no actual test data have been obtained. The continuing close monitoring of this program should be a high priority for RSSHM development.

As shown in Figure 5.15b, the infrared radiation is measured with an interferometer, and the spectrum is obtained by digitizing the interferogram and taking its Fourier Transform. The Fast Fourier Transform algorithm is employed to speed the last process. The hazardous material is then identified by employing either the Simplex algorithm described in subsection 5.4.2.2, or by the alternate detection algorithm described in Section 5.4.3. This alternate algorithm is better suited to the detection of a large list of materials than the Simplex algorithm, but so far it has only been utilized in laboratory environments. It will be necessary to perform some tests to determine if the alternate algorithm can be adapted to the hazardous material detection environment. Both algorithms can readily be implemented with existing digital microcomputer technology. Only one of the algorithms will be incorporated into the final system, and all of the programming will be built into the system. It will not be necessary for the operator to learn computer programming.

The 8-12 μm portion of the infrared spectrum was selected because most of the hazardous materials listed in Table 4.1 have significant spectral components in this portion of the spectrum. This spectral range also coincides with a well-known atmospheric window. Both the single-ended and the double-ended versions of the proposed RSSHM employ thermal, non-laser sources, and the blackbody radiation at normal temperatures is much stronger in this portion of the spectrum than it is in the visible portion of the spectrum. Thus, the detector signal levels are orders of magnitude larger when the 8-12 μm position of the system is utilized.

The use of a visible laser source has been discarded for several reasons. The primary reason is the safety problem involved in having a laser radiate into the surrounding landscape while being manipulated by an operator with limited training. All of the laser-based remote-sensing systems for pollution monitoring, etc., (Section 5.2) have been operated by highly-trained personnel. Another reason for rejecting laser-based systems, which is nearly as important as the preceding reason, is that a suitably rugged, tunable laser has not yet been developed. A tunable laser would be required because of the large variety of hazardous substances which must be investigated. Such a laser would need to be immediately operable by a fireman even after the RSSHM had been sitting idle for years.

The cost of the system should be several thousand dollars in production quantities, and it should weigh in the neighborhood of fifty (50) pounds. These calculations are based upon estimates of the cost and weight of the XM21 which is similar in design to the proposed RSSHM. The cost of smaller-quantity prototypes would be higher, but it is anticipated that by adapting components from the XM21 system these development costs can be minimized. Some suggestions for proceeding with the development of an RSSHM are presented in Section 8.0.

6.0 INSTRUMENTATION TECHNIQUES WHICH DEPEND ON SAMPLING

6.1 Introduction

In principle, the task of identifying a material once a sample of that material has been obtained is much easier than identifying a material remotely. The methods by which a material can be identified by sample analysis are also more numerous and varied than those available for remote detection. In this section, the principal methods of identifying and quantifying materials by sample analysis will be reviewed. Because of the multiplicity of detection techniques and instruments developed in some areas, this review will not attempt to be exhaustive. We have tried, however, to select the main methods for identifying materials with emphasis on those showing some potential for application to the hazardous materials problem. Emphasis was also placed on instruments which have reached production or state-of-the-art status. For instrument types where numerous different manufactured models exist, we have tried at least to give detailed information and references on representative models.

Instruments to be reviewed in this section include those developed for industrial air quality monitoring, atmospheric and water pollution studies, and fire or other emergency applications. Though a number of instruments have been developed for application specifically to hazardous materials, none has been designed for the exact application which is the focus of this study. That is, an instrument for use by the first people at the scene of an accident to rapidly and reliably identify (and ideally quantify) a material out of a large number of possibilities. Thus, though development efforts would be less extensive for non-remote than for remote instruments, some development would be required for any instrument type to be useful for a wide range of hazardous material emergencies.

All of the instruments discussed in this section require that some type of sample of the material be obtained. This would generally imply close access to the material by an emergency

worker. For hazardous, especially poisonous, materials, the requirement of protective clothing and possibly self-contained breathing apparatus is obvious. This study has not included a detailed evaluation of protective clothing types and their effectiveness. However, it should be remembered in the discussions to follow that applications for these instrument types, as distinct from remote instruments, will generally require protective clothing. For some of the instrument types, the possibility of obtaining a sample in a semi-remote manner, for example, through a tube, will be considered at a qualitative level. In any case, for the instruments discussed in this section, the proximity required to the hazardous material will be greater than for remote detection.

In the following subsections, the principal direct sampling techniques will be discussed, beginning with spectroscopic techniques, which bear a resemblance to some of the remote methods discussed in Section 5.0, then proceeding to other methods, roughly in order of their decreasing applicability to a wide variety of hazardous material situations.

6.2 Review of Current Techniques

6.2.1 IR, Visible, and UV Absorption

A number of different techniques follow basically the same procedure of passing a beam of radiation through a sample of material (usually, but not always, gaseous), and measuring its attenuation or absorption. There are significant differences, however, from one technique to another in the spectral range used and in the mode of detection, differences which bear in important ways on multi-hazardous material applications.

6.2.1.1 Nondispersive and Discrete Frequency Instruments

A nondispersive instrument is one which avoids the use of dispersive optics such as prisms or gratings. Nondispersive analyzers generally use broad-band radiation sources, and instruments exist which operate in the infrared, visible, and ultraviolet wavelength ranges.

Because they operate with broad-band sources, nondispersive instruments are sensitized or calibrated for particular materials by means of special filters, gas correlation cells, or calibration curves. Thus, a nondispersive instrument is designed to detect quantities of one known material, or at most, a small number of predetermined materials.

A number of commercially available instruments designed for industrial environment or pollution monitoring exist. For example, Infrared Industries Incorporated, manufactures the 700 Series of infrared gas analyzers for continuous monitoring of specific gases in a sample stream (85). Models IR-703 and IR-705 monitor single species, and Model IR-702 monitors two separate gases. Calibration of specific gases is achieved by an internal optical filter, different for each gas. The DuPont 460 Gas Analyzer System operates over the visible and ultraviolet range (86, pp. U-126 to U-127). The system uses a technique similar to the differential absorption method described in Section 4.2.1.2, and is designed for the two specific gases, SO_2 and NO_2 , with appropriate optical filters built in. CEA Instruments, Inc., manufactures a nondispersive analyzer, the PERCO II, which operates in the IR or UV range, and can monitor up to four gases simultaneously (87). This instrument contains a rotating filter wheel with separate filters for each gas to be analyzed. The limitations of using separate filters for analyzing a large number of materials are obvious; however, the possibility of a continuously variable filter suggests itself, an approach which is, in fact, used in the dispersive analyzer to be discussed in Section 6.2.1.2.2.

A technique called gas-filter correlation has been used with nondispersive systems to make measurements of specific gases. Basically, in this technique the source beam is split by a chopper to pass alternately through a pre-filled cell containing the species to be measured, and through a vacuum or neutral filter cell. The two beams are then passed through the sample to be measured, e.g., across the effluent of a smoke stack. Since the beam that has passed through the correlation cell has already

been attenuated, it will receive little additional attenuation from the species of interest, whereas the other beam will. Thus, the differences in attenuation can be related to the concentration of the target species in the sample. A variation of the gas cell correlation technique is used in the Model 5000 Stack Gas Analyzer manufactured by Environmental Research and Technology, Incorporated (86, pp. U-111 to U-113). This nondispersive IR system is designed to monitor sequentially up to four gas species present in stack effluents, typically SO_2 , NO, CO_2 , and CO. W.F. Herget has described a gas-filter correlation instrument utilizing dispersive rather than nondispersive techniques to improve the discrimination and stability of the instrument (88). This instrument is still limited to a relatively small number of predetermined species through the necessity of having a series of prepared gas-filter cells. In principle, it would be possible to adapt the gas-filter cell correlation technique to identifying unknown hazardous materials by manually or mechanically stepping through a large number of prepared correlation cells containing samples of many hazardous materials. Such an approach would seem to be very cumbersome, however, and unattractive in view of other simpler possibilities to be discussed in later sections.

Rather than using broad-band sources, it is possible to use single or discrete frequency sources for absorption measurements. Such instruments could still be considered nondispersive in that they do not use gratings, prisms, etc., to select specific wavelengths. This class of instruments would include laser monitors which are used in situ, or on an obtained sample of material rather than remotely.

Examples of the use of lasers for non-remote measurements include work at NASA-Langley monitoring CO from an aircraft (89). In this application, a tunable diode laser beam is passed along a 10-meter absorption path in the airstream next to the fuselage of a C-54 aircraft. Sensitivities on the order of 20 parts per billion are reported. A. Tönnissen, et al, in Germany,

have recently reported laser measurements of hydrogen fluoride made in situ in the loft of an aluminum plant (90). A group in Canada under J. Reid, using a tunable lead-salt diode laser and a multi-pass White cell, has reported measurements of SO_2 on the order of 3 parts per billion (49). With their tunable laser, they claim they can achieve detection of other common atmospheric species such as N_2O , H_2O , CO_2 , and O_3 . Their laser, though tunable, covers the relatively narrow range of 1050 to 1150 cm^{-1} , and thus would not be adaptable to a wide variety of hazardous materials.

These laser techniques have been pursued with an emphasis on the ability to achieve high sensitivity through the use of well-defined beams and high resolution optics and detection systems. Though used for in situ measurements, these are precision instruments, intended for use by trained technicians. More significantly, these laser instruments have been designed for single species, or at best, when tunable lasers are used, for a relatively small group of materials. Thus, the applicability to a wide range of hazardous materials does not seem promising.

All of the techniques discussed in this subsection, then, suffer from the shortcoming that they are specific to one material or, at most, a few materials. Though very useful for specific industrial or pollution applications, these measurement techniques show little potential for application to hazardous material detection.

6.2.1.2 Dispersive Absorption Instruments

In contrast to the nondispersive instruments described in the preceding section, dispersive instruments allow the source of radiation to be set at any wavelength over a relatively broad range within the design limits of the instrument. The dispersive element may be a prism, a grating, or a variable filter.

Because of the possibility of scanning the radiation source over a wide range, and hence of measuring a broad portion of the absorption spectrum of a material, the potential exists

for using a dispersive instrument to discriminate one material from another. A number of commercial dispersive instruments exist which can, indeed, be used to make measurements of a wide variety of materials. No instrument, however, has been developed specifically for the purpose of identifying an unknown hazardous material. Moreover, as far as could be determined in this study, only one line of instruments, the Foxboro-Wilks MIRAN series, has been designed to be truly portable. In the subsections to follow, several non-portable instruments will be briefly described. The MIRAN-type instrument and its possibility for future development will then be discussed in further detail.

Before discussing specific instrument types, a few comments should be made about the choice of wavelength range in which an instrument might operate. Both nondispersive and dispersive instruments have been designed for the infrared, visible, and/or ultraviolet regions. Most materials show absorption over the entire IR-UV range. In the infrared region, however, the spectral structure is generally due to vibrational/rotational changes of molecules in their electronic ground states. At higher energies, in the visible and ultraviolet regions, the spectral features are due to valence-shell electron transitions, with superimposed vibrational/rotational fine structure. For molecules, the spectral features in the visible/ultraviolet regions tend to be somewhat more complex, or less distinctive of a given species. Moreover, interferences from other molecules tend to be more difficult to sort out. This difficulty has led to the development of second-derivative, or higher order, analyses of UV spectra for improved detectability of overlapping lines. On the other hand, since photons in the ultraviolet are higher in energy, detection sensitivity problems are somewhat less severe than in the infrared. The choice of instrument design, therefore, is a matter of both spectral features and individual component choice. The fact that instruments have been designed for all three regions shows that IR, visible, and UV all have their applications. All other things being equal,

however, the IR spectral region seems to be more attractive for application to a wide range of materials.

6.2.1.2.1 Non-Portable Dispersive Instruments

Lear Siegler, Inc., manufactures an instrument called a second derivative spectrometer (86, pp. U-129 to U-130). This instrument processes the transmission versus wavelength function of a scanning single-beam spectrometer to produce a signal proportional to the second derivative of this function. This processing enhances the signal-to-noise ratio and the resolution of the data. The Lear Siegler SM400 covers the wavelength range of 200-600 nm in the visible and UV range. The spectral resolution claimed is 0.4 nm.

This instrument is intended for laboratory use. With a weight of 132 pounds, it does not lend itself to use as a portable instrument. Emphasis is on high sensitivity, with concentrations in the parts-per-billion range detectable.

In its present form, this second derivative spectrometer would not be suitable for first-on-the-scene application to hazardous material emergencies. However, there could be some value for an instrument such as this in the intermediate or late timeframe of an accident. Possible uses would include identification of constituents in mixtures of materials, for example, where chemical wastes were involved, or where loads from several railroad cars were combined in an accident. The high sensitivity of this instrument might also be useful during cleanup operations.

Beckman Instruments manufactures a series of spectrophotometers that operate throughout the UV, visible, and near-IR ranges (91). These are laboratory instruments designed for detailed analyses of air, water, or biomedical samples. The 5200 series covers the wavelength range of 190 to 3000 nm in one instrument, with separate sources and detectors to reach this entire range. Resolution claimed for the most advanced model is less than 0.05 nm from 190 to 800 nm, and less than 0.3 nm from 800 to 3,000 nm. Lower detectable limits are listed as 1-10 ppb. Another model, the DU-8, comes equipped with a microcomputer data

processing system. With weights in the range of 190 to 290 pounds, these instruments are heavier than the second derivative spectrometer. They are relatively expensive, with prices ranging from \$15,800 to \$29,000 (1976 prices) for various models. Thus, these instruments would be useful for many laboratory applications, but would probably be too sophisticated for use by an emergency team.

6.2.1.2.2 Portable Dispersive IR Instrument

The Wilks Infrared Center of Foxboro Analytical manufactures a series of truly portable dispersive IR analyzers (92) called by the trade name MIRAN (Miniature InfraRed ANalyzer). A number of models of MIRAN analyzers have been developed for various specific uses, including one, the MIRAN-80, with a built-in microprocessor. Compared to other non-remote, radiation-absorption instruments evaluated in this study, an instrument of this type shows the most promise for development as a hazardous material detector.

Table 6.1 compares features of the various models of MIRAN analyzers. The MIRAN-101, designed for one specific gas, and the MIRAN-103, with interchangeable filters, would have little application to a large number of hazardous materials, and will not be considered further. The discussions to follow will refer, for the most part, to the MIRAN-1A or -80 models.

A photograph of the MIRAN-80 with gas sample cell is shown in Figure 6.1, and a schematic diagram is given in Figure 6.2. The MIRAN-1A would have the same general arrangement, except for the absence of the microcomputer component. The MIRAN-1A, however, does have provision for the output to be fed to a strip chart recorder, so that a permanent record of the entire IR spectrum of a material can be made. The MIRAN-80 can be used to analyze liquid or thin solid samples with the substitution of appropriate sample-handling devices for the long gas sample cell shown in the diagram.

The MIRAN-1A and -104 can be set at a fixed wavelength for continuous monitoring of a specific substance, or the beam

Table 6.1 - Comparison of Models of MIRAN Analyzers

MODEL	FEATURES	SENSITIVITY (ppm)	WEIGHT (lb) (kg)		COST
MIRAN-101	For one specific gas or vapor only.	~1	18	8.2	\$3647
MIRAN-103	Can be used for more than one material by change of filter and meter scale.	~1	23	10.4	\$4987
MIRAN-104	Circular Variable Filter allows multi-material capability; wavelength range - 2.5 - 14.5 μ m.	~1	24	11.0	-
MIRAN-1A	Same as 104, but with sensitivity a factor of 2 higher.	< 1	32	14.0	\$7303
MIRAN-80	Same as 1A, but with microcomputer capability.	< 1	52 30	23.6 13.6	\$14,375 (without gas cell)



Fig. 6.1 - MIRAN 80 Analyzer With 20-Meter Gas Cell
(Used with permission of Foxboro Analytical)

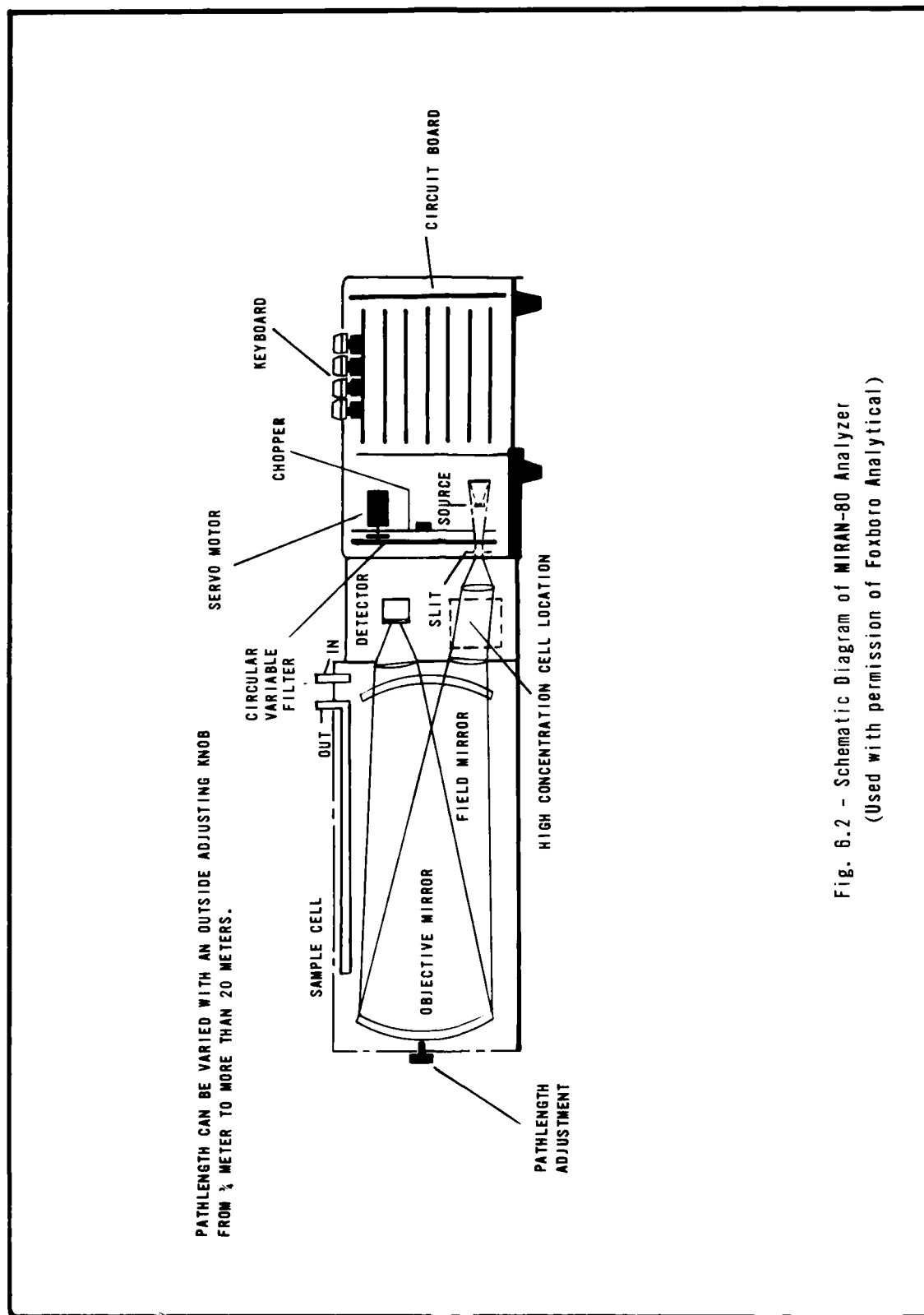


Fig. 6.2 - Schematic Diagram of MIRAN-80 Analyzer
(Used with permission of Foxboro Analytical)

can be scanned manually or automatically to cover its entire 2.5 to 14.5 μm range. The MIRAN-80 can be set to scan the entire spectral range at speeds varying from 8 to 30 minutes for a full range scan.

A key feature of the MIRAN-1A, -80, and -104 is the circular variable filter which selects a narrow wavelength range from the broadband IR radiation emitted by the nichrome wire source. This is an interference filter with a film of varying thickness designed such that it permits radiation of different wavelengths to pass through, depending on its angular position (80). In the design selected for the MIRAN instruments, three separate segments are used to span the wavelength range of 2.5 to 14.5 μm . The approximate wavelength resolutions claimed by Foxboro for the MIRAN-80 set at a 0.5 mm slit width (minimum setting) are as follows:

0.05 μm at 3.5 μm wavelength
0.08 μm at 6 μm wavelength
0.22 μm at 12 μm wavelength

The fact that the MIRAN-80 has a microprocessor capability is significant for application to hazardous material identification. The principal intended use for this instrument is the quantitative analysis of multi-component mixtures. In a typical application, the main wavelengths of several known components of a mixture are entered as data, and the instrument calculates, from the measured absorption spectrum, the percentage of each component present. However, other types of analysis are possible, within the limits of the computer memory, including spectral identification or pattern recognition. Extensive analyses are now performed with the aid of an external computer system; however, for hazardous material pattern recognition problems, an extension of computer capacity to allow self-contained analytical operations would be desirable.

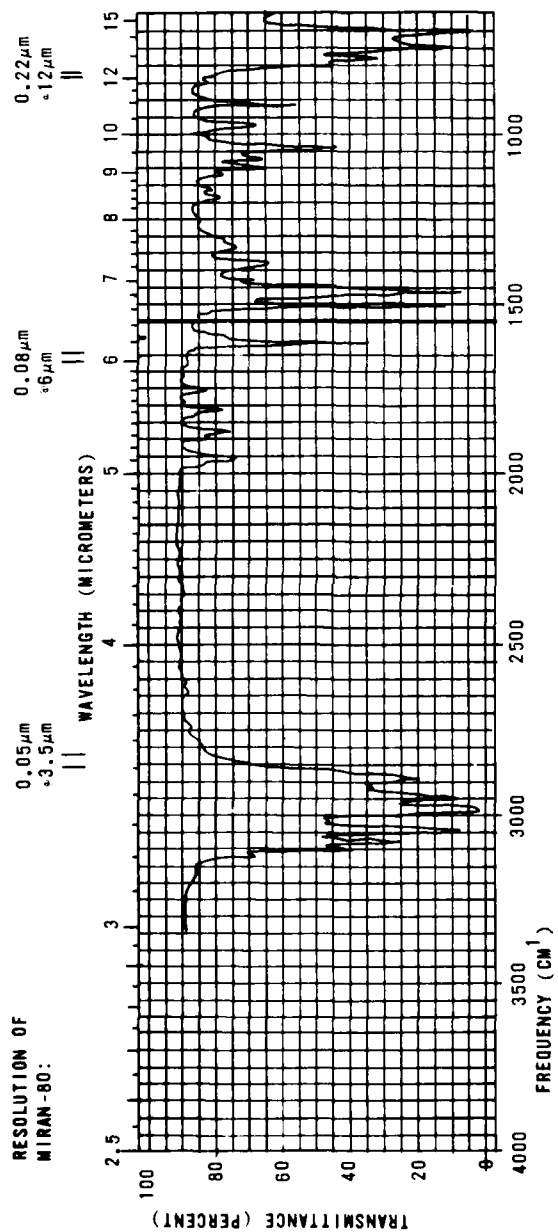
The microcomputer component of the MIRAN-80 is an INTEL 8080A with 5K of PROM (Programmable Read Only Memory) and 1K of RAM (Random Access Memory) (93). These are relatively

modest capabilities for a microprocessor. Within the present design of the INTEL 8080A, the limit on memory should be 64K. Beyond that, the possibility exists of going to peripherals such as floppy disks or mini-floppy disks.

To develop this instrument for hazardous material detection, several aspects must be considered: the resolution of the instrument and its capability to discriminate one material from another; the methods by which one might get the hazardous material into the analyzer; and the development of software and hardware for the discrimination subsystem.

The values of resolution of the MIRAN-80 at three different wavelengths have been quoted previously. These values are compared with the IR absorption spectrum of a material with relatively fine spectral structure in Figure 6.3. As can be seen, the resolution widths are slightly broader than the half-widths of some of the peaks for this material, ethyl benzene. Therefore, a spectrum of this material measured by the MIRAN-80 would not show such narrow, sharp peaks. Nevertheless, these resolution values would be sufficient to separate the major, and most of the minor, peaks in this spectrum. Such a measurement would result in lower, broader, yet generally distinct peaks centered at the same wavelengths as those shown in Figure 6.3. Thus, the present design would seem sufficiently precise to distinguish one material from another for most of the materials whose IR spectra were gathered. Background interferences and interferences from mixtures of materials would, of course, complicate the picture. In any development effort, the precise limits on detectability for various backgrounds and for any specific material should be determined. Also, improvements in the design for better resolution could be investigated.

A MIRAN-type instrument could be operated by a worker dressed in protective clothing and approaching a vapor cloud or pool of volatile liquid. It could also be used, with proper sample handling techniques, on non-volatile liquids, and even solids. In these instances, minimal or no protective clothing might be required. Also, bringing a gas or vapor to the



ABSORPTION SPECTRUM OF ETHYL BENZENE (C_8H_{10})

Adapted from Coblenz Society Spectrum #3577 (22) with permission.

Fig. 6.3 - Comparative Resolution of MIRAN-80

instrument by means of a long sampling tube, so that it could be used in a semi-remote manner, is a very real possibility. The present MIRAN-104, -1A, and -80 designs have flexible inlet tubing, particulate filters, and air pumps to pull samples through and purge the gas cell. Sample collection distances up to 30 meters are cited. With enlarged diameter tubing and/or more powerful pumps, larger sampling distances should be achievable. One can imagine an explosive device to fire a line of flexible tubing into a potentially hazardous vapor cloud from a safe distance. Experimental studies of such a semi-remote sampling system should be a part of any development effort on an instrument of this type.

The discrimination subsystem for a MIRAN-type instrument applied to hazardous material detection would be very much like that discussed for the XM21 remote system in Sections 5.4.2.3 and 5.4.3. Of course, the question of whether or not to perform a Fourier transform would not apply here, since one would be working directly with an absorption spectrum. Other differences in the quality of the data to be processed are that, although the resolution would be poorer than for the remote, interferometer design*, signal-to-noise ratios would be higher since one would be working with an internal radiation source and a direct sample. Atmospheric interferences would still be a concern since sample spectra would not be measured in a vacuum, but the interference effects should be less severe since the radiation signal would not travel the long distances of a remote instrument, but only the path length of the gas cell. Thus, background interferences should present less of a problem in the development of a discrimination algorithm. As noted above, the potential

*The question might be raised, "Why not adapt an interferometer design to a non-remote instrument as well as to a remote instrument?" The answer is that such an application is possible, but the high throughput of an interferometer is not required in such an application. The needs for the spectrum analyzer in a non-remote instrument can be met by a simpler and less sophisticated approach.

for increasing the memory capacity of the microcomputer over the present INTEL 8080A unit exists. The exact requirements on the computer would depend on the details of the discrimination algorithm selected.

One final word should be said about costs. The MIRAN instruments are not inexpensive, as the approximate costs listed in Table 6.1 indicate. However, no instruments designed for the sophisticated tasks proposed in this study are likely to be cheap. Although such an instrument would not be within the budget of every small volunteer fire company, it would not be out of reach for larger companies in larger cities where the number of hazardous material accidents would be greater, and the use of such an instrument more frequent. Given the present cost of the MIRAN-80, costs of an instrument with a more elaborate discrimination/microcomputer subsystem should not be significantly higher, assuming that development costs would be covered in part by government grants. The costs for chips or boards for added ROM or RAM units is on the order of hundreds of dollars or less per unit, and software development costs are on the order of thousands of dollars, spread over the number of units produced. Thus, cost increases for an instrument adapted for hazardous material use could be expected to be on the order of tens of percents rather than factors of two or three.

In summary, at the level of evaluation possible in this study, the portable MIRAN-type infrared analyzer seems to be a viable instrument for application to hazardous material detection, granted the acceptance of the requirement for obtaining a sample of the material. The major development work needed is the design of the discrimination subsystem.

6.2.2 Mass Spectrometry

6.2.2.1 Background

One straightforward way of identifying a material is by a precise measurement of its mass or, more specifically, its charge-to-mass ratio. One advantage of mass spectroscopy is that it can detect any particle which can be ionized, and does

not have limitations on certain types of molecules as with symmetrical diatomic molecules for IR detection. This advantage, however, is balanced somewhat by the fact that mass spectrometry does not distinguish between substances with the same atomic weight, but differing in chemical formula. Many different designs of mass spectrometers have been pursued by the scientific community for a variety of applications. This section will concentrate on the specific possibilities of mass spectrometry as applied to the multi-hazardous material problem, with emphasis on portable instrumentation.

The various types of mass spectrometers all depend in some way on the action of charged particles of a certain mass in electromagnetic fields. Thus, any mass spectrometer will have an ion source, or device to ionize the materials to be detected, a mass filter of some sort, and a detection system which may be either photographic (this method would not apply to a portable instrument) or electrical, e.g., by an electron-multiplier detector. The mass filter may be of various types, three of the most common being sector magnets, quadrupole units, and time-of-flight devices. With the "standard" sector magnet, particles are accelerated or sorted to have the same kinetic energy, then passed through a uniform magnetic field in which particles of different masses will travel paths with different radii of curvature. In a quadrupole mass spectrometer, an RF oscillation across a quadrupole electrode allows particles of only a certain mass to pass through, depending on the applied voltage and frequency. A time-of-flight device accelerates charged particles across a given voltage, and allows them to pass through a drift region from which the lighter, faster particles emerge sooner than the slower, heavier ones. The choice of a type of instrument is a function of sensitivity, size, weight, and type of application. A quadrupole mass spectrometer has a linear mass scale, convenient for data processing and analysis. The quadrupole analyzer itself tends to be more compact than the sector magnet, especially for a wide range of atomic mass units (AMU's); however the associated electronics add weight and complexity which the sector magnet does not require. A time-of-flight unit, though relatively bulky, has the advantage that the mass filter

unit (drift tube) is very simple and easily cleaned, even with dirty compounds.

In principle, mass spectrometers have certain design features which militate against their being used as portable instruments. They must operate in a vacuum requiring a separate vacuum system, which can be bulky and heavy. For the best resolution, a cryogenic system would be required. However, a trade-off can be made for less resolution and a less elaborate vacuum system. Also, the mass filter portion is typically heavy and/or bulky. Magnets or electrodes are heavy, and certain travel distances are required to determine radii of curvature or time-of-flight. Nevertheless, attempts have been made to miniaturize various components, and to develop mass spectrometers into portable instruments. Two of these efforts will be described in the latter part of the next section.

6.2.2.2 Specific Instrument Types

Two applications of mass spectrometers for hazardous material detection, though not for use as portable instruments, will be described first.

CVC Products, Inc., has developed a time-of-flight mass spectrometer, the SUPERSPEC 600, for the analysis of gases in industrial processes (94). This is a rack-mounted unit with a sensitivity in the 5 ppm range. It covers a mass range of 1 to 600 AMU (with a possibility of extension to 1000 AMU for research applications), and includes a multicomponent monitoring feature allowing simultaneous monitoring of up to six species. Information can be displayed on standard oscilloscopes or strip recorders. Though the instrument appears to be very versatile for industrial applications, its size and weight preclude consideration for portable use. The vacuum and analyzer console alone, for example, weighs 150 pounds. Nevertheless, an instrument of this type might find some application for intermediate or late-time analysis in hazardous material emergencies.

In another application, UTI, Inc., has developed a quadrupole mass spectrometer for analyzing hazardous gases in

NASA's Space Shuttle project (95). Specifically, the system is designed to monitor, in an automated mode, gases drawn from various compartments of the Space Shuttle during fueling operations. Emphasis was placed on the ability to meet a wide variety of severe environmental conditions associated with launch operations not normally encountered in a laboratory. For example, the system combines high sensitivity--the ability to detect 0.13 ppm of Krypton 83 in the air--with a capability of measuring and storing data on 8 different constituents. Though this system, like the one previously described, is not portable, the technology for meeting severe environmental conditions could find some application should development of a portable mass spectrometer for hazardous material applications be pursued.

More important than the two instruments described above are two programs aimed specifically at developing technology for lightweight, portable mass spectrometer instruments.

The first program is a contract with Analog Technology Corporation sponsored jointly by NASA, EPA, and DoD, with NASA Langley assuming primary technical direction responsibilities (96). The key aspect of this program was the development of a very small, 5.1 cm long, yet precisely shaped, tungsten hyperbolic quadrupole unit, manufactured by a chemical vapor deposition process. The system is designed for a mass range of 4 to 200 AMU (less than the range of the CVC instrument) and a sensitivity on the order of 2 ppm.

This project is the outgrowth of a previous NASA contract to design a miniature quadrupole mass spectrometer complete with vacuum system and electronics, and small enough to be carried by an astronaut for continuous breath analysis (96, p. 3). In the system developed under this contract, however, the vacuum system technology was not sufficient to produce a truly portable, hand-held instrument. In its present state, the system is contained in two rack-mounted units, and weighs approximately 200 pounds (97). The difficulty of achieving light weights underscores one of the inherent problems of mass spectrometers. Though

not hand-portable, the present system could be mounted in a van for intermediate-time applications. Future advances in vacuum system technology may permit the achievement of lighter weights. The present joint NASA, EPA, DoD project is still underway, and should be monitored by FEMA for possible applications to hazardous material detection.

A second NASA-related effort at developing a portable mass spectrometer system is being carried on at the Cal Tech Jet Propulsion Laboratory. A Systems Definition and Feasibility Study under the direction of Dr. Charles E. Giffin will draw upon the technology and hardware developed for the 1975 Viking Mars Lander Mission. As a part of this mission, a small-sized, light-weight mass spectrometer was designed to analyze Martian soil samples and the Martian atmosphere at the surface. A detailed discussion of all components of the Viking instrument is given in Reference 98. This instrument, containing a sector magnet mass spectrometer, covered a mass range of 12-215 AMU. The light weight of this instrument was achieved in part because of the relatively small mass range for which it was designed (the mass range below 12 AMU would be more accessible to a quadrupole instrument), and the fact that this type of instrument does not require the electronics necessary for an RF quadrupole head. The Viking instrument also employs a technique to allow the permanent magnet to do double service as the magnet for the ion source vacuum system, as well as for the mass analyzer. Two instruments of this design were successfully placed on Mars and made numerous soil and atmospheric analyses through April of 1977.

The current feasibility study will aim at producing two prototypes of completely portable, valise-sized units for in situ sampling and analysis in hazardous material spills (99, 100). Specifically, two backup flight-configured Viking Lander instruments will be modified for this portable configuration. A photograph of a mock-up of this configuration is shown in Figure 6.4. The goal for the weight of this portable system is 30 pounds. Proposed plans include a data tie-in with the main computer at Cal Tech.

This program is ongoing, in its very early stages as of this writing, and no details of performance in the new configuration are available. However, it is one of the few known

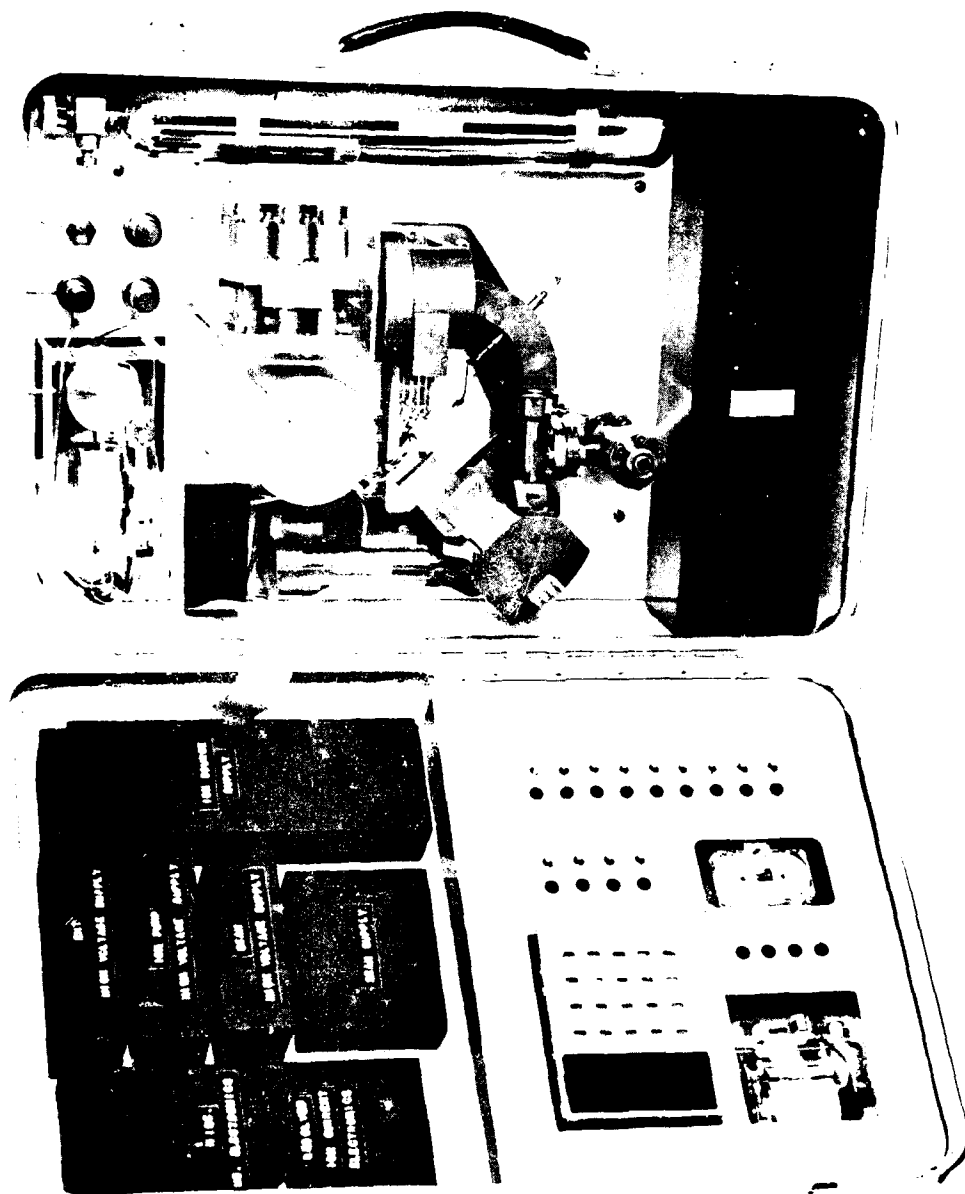


Fig. 6.4 — Mock-Up of Proposed Portable Mass Spectrometer
 (" Provided through the courtesy of the National Aeronautics
 and Space Administration, Jet Propulsion Laboratory, California
 Institute of Technology ")

programs aimed specifically at developing a portable instrument for broad application to hazardous material emergencies. Granted that the instrument is not remote, it ought to be very useful to emergency personnel should it prove successful. The program should be closely monitored for experimental results as they become available, since this instrument would have a direct application to FEMA emergency missions.

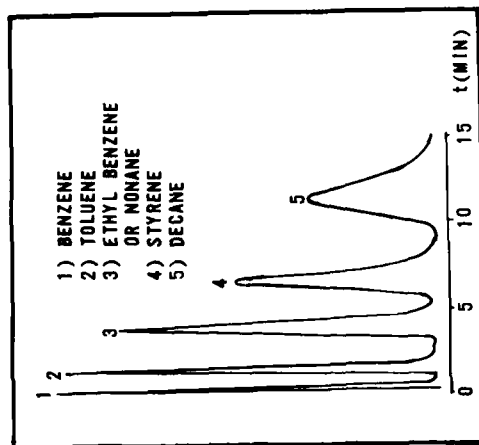
6.2.3 Gas Chromatography

6.2.3.1 Background

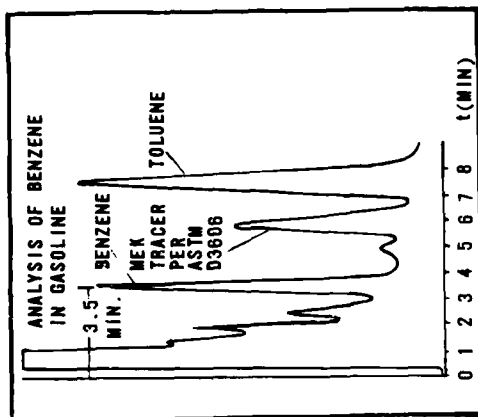
As with mass spectrometers, gas chromatographs are instruments which have seen a wide variety of applications for laboratory use. Recently, a number of portable instruments have been built. This section will briefly discuss some of the principles of gas chromatography, and then will present information on several commercially-available portable models.

A gas chromatograph (GC) basically separates components of a gaseous mixture. In such an instrument, gas and vapor samples are carried through specially prepared columns, often by an inert carrier gas such as helium. The columns contain a packing or lining material which serves to separate the sample mixture into its individual component chemical species. The components travel through the column at different rates, emerging from the end of the column at different times. A detector, which is not specific to particular chemical species, detects the arrival of the components, and records or stores this information. A gas chromatogram, then, consists of a tracing of intensity versus time, with individual peaks representing individual components of the original gaseous mixture. Examples of three chromatograms are shown in Figure 6.5.

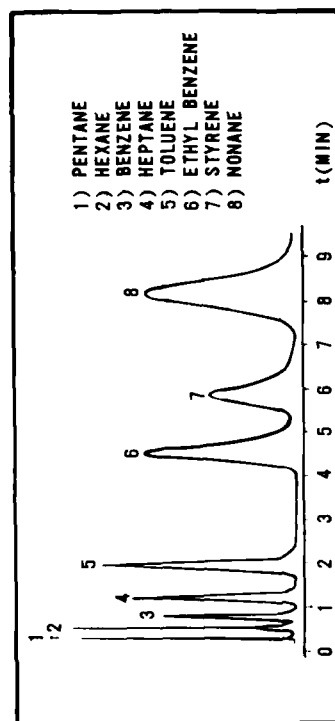
One significant aspect of gas chromatographs as they relate to hazardous material detection is that the separations produced in the chromatogram are very much a function of the type of column, the length, and the type of packing material. Referring again to Figure 6.5, one can see that the two common materials, Benzene and Toluene, elute at different times in each



6.5a 12" B Column



6.5b 24" T Column



6.5c 24" G Column

COLUMNS

- B- 3% DIODECYL PHTHALATE ON CHROMOSORB W, AW, 60/80 MESH
- G- 10% SP-2100 ON SUPELCOPORT, 60/80 MESH
- T- 10% 1, 2, 3-TRIS (2-CYANOETHOXY) PROPANE ON CHROMOSORB P, AW, 60/80 MESH

Fig. 6.5 Typical Gas Chromatograms
Reference 101, used with permission

chromatogram. That the difference is due not just to the length of the column can be seen by comparing 6.5b and 6.5c, both of which reflect data for 24" columns, but with different packing materials. Moreover, no one packing material will react with all chemical species. Different columns or packing materials are selected for different groups of chemicals. A given chemical may be detectable with more than one column, as seen in Figures 6.1a, b, and c, but columns are chosen for their sensitivity to groups of species often encountered together.

Thus, for a large number of hazardous materials, a family of columns would generally be employed, and the instrument needs to be calibrated for the various combinations of materials and columns. This aspect makes gas chromatographs less than desirable for the identification of an unknown hazardous material. Where such an instrument could be very useful would be in situations where complex mixtures are encountered, for example, in wrecks where many cars or containers are jumbled together, or in incidents involving hazardous wastes where unknown mixtures are present. A GC is more likely to be useful in the intermediate time frame of a hazardous material accident. If used by the first-on-the-scene emergency worker, its application may be relatively time-consuming.

6.2.3.2 Specific Instrument Types

Some instruments using gas chromatographic separation techniques have been designed to analyze only a few materials, for example, to separate sulfur-containing pollutants from air samples. Other instruments have been designed for a wider variety of applications. In the following paragraphs, portable instruments applicable to a large number of materials will be discussed.

Data for four different commercial instrument series are compared in Table 6.2. Because of its very light weight, 12 pounds, and features such as total organic vapor concentration indicator and audible alarm, the Century Systems instrument would be the most useful for early-on-the-scene analysis where

Table 6.2 - Comparison of Portable GC Instruments				
CENTURY SYSTEMS DIVISION OF FOXBORO ANALYTICAL (Ref. 101)		GOW-MAC (Ref. 102)	ANALYTICAL INSTRUMENT DEVELOPMENT, INC. (Ref. 86, U-163 to 164; Ref. 103)	UNICO-NATIONAL ENVIRONMENTAL INDUSTRIES, INC. (Ref. 86, U-78 to 80)
INTENDED USE	ORGANIC VAPOR ANALYSIS	LAB USE: ARSON DETECTION	AIR POLLUTION AND ENVIRONMENTAL HEALTH STUDIES	FIELD ANALYSIS OF TRACE GASES AND VAPORS
COLUMNS	INTERCHANGEABLE COLUMNS WITH 5' PACKINGS. IN 9", 12", AND 24" LENGTHS	VARIETY OF COLUMNS PACKED TO ORDER. CAN ACCEPT COILED COLUMNS 25" TO 50" IN LENGTH	ACCEPTS VARIETY OF METAL, GLASS, AND TEFLON COLUMNS IN 20', 12', AND 36' LENGTHS	SEPARATE COLUMNS AVAILABLE FOR 27 DIFFERENT MATERIALS
CARRIER GAS	HYDROGEN	HELIUM, HYDROGEN OR NITROGEN	HYDROGEN, AIR OR OTHER	HELIUM
DETECTOR TYPE	FLAME IONIZATION	FLAME IONIZATION OR THERMAL CONDUCTIVITY	FLAME IONIZATION, FLAME PHOTOMETRIC, ELECTRON CAPTURE OR THERMAL CONDUCTIVITY	THERMAL CONDUCTIVITY
RECORDER	PORTABLE STRIP CHART RECORDER AVAILABLE	SEVERAL MODELS OF STRIP CHART RECORDERS AVAILABLE AS ACCESSORIES		BUILT-IN UNICORDER STRIP CHART
TEMPERATURE CONTROL	TEMPERATURE CONTROL PACK AVAILABLE (0° TO 100°C)	COLUMN OVENS GIVE RANGE OF AMBIENT TO 400°C	COLUMN OVEN GIVES RANGE OF AMBIENT TO 200°C	THERMOSTATICALLY CONTROLLED HEATER MAINTAINS TEMPERATURE AT 50°C
SENSITIVITY	< 1 PPM TOTAL ORGANIC VAPOR	10 ⁻¹² G/SEC HYDROCARBONS		20-170 PPM, DEPENDING ON MATERIAL
WEIGHT	12 LB (5.5 KG)	40-48 LB (18-22 KG)	36-40 LB (16-18 KG)	49 LB (22.2 KG)
PRICE	\$4200-4900	\$750 ARSON MODEL \$3500 MICROPROCESSOR MODEL	\$3300-4500 (1976 PRICES)	
OTHER FEATURES AND COMMENTS	SEPARATE DIRECT READING OF TOTAL ORGANIC VAPOR CONCENTRATION. AUDIBLE ALARM SET AT SELECTED THRESHOLD. 8 HOUR OPERATING TIME ON BATTERY PACK.	SPECIAL ARSON DETECTION MODEL AVAILABLE. ALSO MICROPROCESSOR-MATED MODEL. NOT SPECIFICALLY DESIGNED FOR PORTABLE USE, BUT LOW IN WEIGHT.	RECHARGEABLE NiCd BATTERIES FOR PORTABLE USE. DIFFERENT MODEL NUMBERS HAVE DIFFERENT DETECTORS.	THOUGH HOUSED IN FIBERGLASS CASE FOR PORTABILITY, REQUIRES 115 V, 60 Hz AC POWER SOURCE.

GC capabilities would be required. The other instruments are heavier, but their longer gas columns would allow finer resolution of gaseous species. As noted, the GOW-MAC Series 5297 is designed with a column specially packed for arson detection.

All of these instruments are potentially applicable to a wide variety of materials. The Century Systems instrument has five columns especially designed for groups of organic vapors, but other columns could readily be prepared. The UNICO instrument description lists 27 specific materials but, again, there is no inherent limit to this number. The other instruments accept a variety of columns, either prepared by the company, or prepared in one's laboratory.

The problem with using a GC for an unknown material is that one should have a general idea of the type of material in order to select the proper column. Manually changing columns in order to investigate a large number of possibilities would be a time-consuming operation. A GC would be most useful in testing for the presence of some suspected substance, or in separating components in complex mixtures, provided one had an idea what the ingredients were, or had sufficient time to step through a large number of possibilities.

One novel application of GC technology which is not yet at production-level, but is near it, is a pocket-sized personnel monitor. Stephen Terry at Stanford University, with support from NASA and NIOSH (National Institute for Occupational Safety and Health), is developing a miniature GC column etched on a silicon wafer and utilizing integrated circuit processing technology (104). The instrument will be a completely self-contained GC, including a carrier gas supply, a microcomputer system for automatic control and data analysis, and an audible alarm, all pocket-sized. The column will consist of a groove 200 μm by 20 μm in cross-section, 1/2 meter long etched in a circular pattern on a silicon wafer 5 cm in diameter. The instrument is designed to monitor up to 10 contaminant vapors in a worker's breathing zone, and to sample the atmosphere once every two minutes for up to eight hours. Estimated detection limits are

10 to 50 ppm. These performance figures are estimated, but prototype models are near completion, with six scheduled for delivery to NIOSH for evaluation. Initial projected retail price is about \$2,000 per instrument.

Should these instruments be able to perform as planned, their usefulness to workers near toxic materials is obvious. Moreover, the miniaturization of components would have wider applications. With such small components and microcomputer control technology, it should be possible to build a small instrument with a relatively large number of different columns. The instrument could be programmed to automatically cycle through a series of steps in order to discern unknown contaminants. Such miniature column/microcomputer technology would eliminate the clumsy manual changing of columns necessary in present GC instruments. Thus, the progress on this type of instrument should definitely be monitored by FEMA for future hazardous material detection applications.

6.2.4 Gas Chromatography/Mass Spectrometry

As implied in the previous section, a gas chromatograph basically separates gaseous constituents, but does not in itself identify them. Identification can be achieved by comparing chromatograms with previously prepared calibration chromatograms for that instrument, or by introducing the separated species into another component for identification. A combination frequently used is a gas chromatograph mated with a mass spectrometer (GC/MS). Typically, in such an instrument, the mass spectrometer can be operated separately, or the two can be used in tandem.

A GC/MS instrument is a versatile laboratory device for the complete qualitative analysis of a complex organic mixture of a multitude of components. The need for such a system in hazardous material emergencies is less obvious. Yet, a miniature portable GC/MS system is feasible, and the possibility is worth some consideration.

A typical laboratory GC/MS system would be the CVC 2001 (105). This system mates a time-of-flight mass spectrometer

similar to that described in Section 6.2.2.2 (94) with a two-column oven-heated gas chromatograph. The system can be used for many laboratory applications, but its size, the width of three laboratory rack units, would preclude its consideration for portable use except possibly as a mobile system in a van.

Much smaller instruments are possible, however. The portable mass spectrometer being developed by Cal Tech/NASA from Viking technology described in Section 6.2.2.2 is, in fact, a GC/MS combination. In the Viking experiments, Martian soil samples were heated in an oven to volatilize organic components. These components were separated in the gas chromatograph, and then analyzed with the mass spectrometer. A general purpose, low-bleed column was used in the Viking instrument. The mass range of this smaller instrument, 12 to 215 AMU is, of course, less than that of a laboratory instrument, 1 to 1000 AMU; however, this range would allow detection of molecules with up to seven or eight carbon atoms. One important question that must be answered in the development stages of this portable instrument is what column, or combination of columns, would be required for wide hazardous material application. The general-purpose column used in the Martian instrument was estimated by JPL personnel to be capable of detecting 90-95% of the materials in the OSHA list. What one gives up in a general-purpose column is resolution and the possibly shorter elution time of a more specific column.

As indicated by the discussion above of the pocket-sized GC personnel monitor, the possibilities of extreme miniaturization of GC units is attractive. On the other hand, with the need for a vacuum system and mass analyzer, there will always be a significant limit to the size of mass spectrometer. To achieve smaller size, one would either give up mass range, resolution, or both. Thus, the question resolves itself into whether, with a given mass spectrometer, the addition of a GC capability is desirable. With advanced technology, the added GC function would be possible with a relatively small increment in size and weight. Thus, to the extent that portable mass spectrometers are seriously considered for development as hazardous material detection instruments, the option of an added GC capability should also be pursued.

6.2.5 Methods Limited to Specific Materials

A large number of techniques exist, many of them depending on chemical reactions of various types, for identifying and quantifying specific materials. Some of these techniques have been incorporated into instruments designed for one or a small group of materials. In other applications, kits have been developed employing a series of different techniques to achieve coverage of a wide range of materials. These kits may include instruments for measuring specific material parameters, for example, pH or conductivity, as partial steps to aid in detection or identification. In the following subsections, kits employing several techniques to detect many materials will first be reviewed, and then instruments designed for limited groups of materials will be discussed.

6.2.5.1 Chemical Kits for Material Detection

6.2.5.1.1 Detector Tubes

Several different companies manufacture detector tubes specifically for certain chemicals, and make these tubes available in kits to allow detection of a variety of materials. These kits might be considered to work on a single "technique"; yet, since the chemical reaction for each tube is different, one could speak of a variety of techniques. The principal manufacturers of such tubes and kits are Mine Safety Appliances Company (MSA), National Draeger, Inc., Bendix/Gastec (National Environmental Instruments, Inc.), and Matheson Gas Products, Division of Will Ross, Inc.

The detector tubes fall under the category of colorimetric indicators, and typically consist of glass cylinders sealed at each end and filled with chemically-treated packings designed to react with a specific gas or vapor. The chemical reactions with the target material produce either a stain of a certain length in the tube, the length being proportional to the concentration of the contaminant, or a color change throughout the tube, the degree of color being proportional to

concentration. For example, in a tube containing silica gel impregnated with a yellow silicomolybdate compound catalyzed with palladium sulphate, the blue-green discoloration in the yellow-colored reagent is proportional to the amount of CO present in the sample (86, p. S-32).

Measurements usually require a detector tube and a calibrated pump to draw a predetermined volume of air through the tube. In typical use, the two ends of the glass tube are broken off, it is inserted in the end of the pump, and the handle is pulled a certain number of strokes to draw the required amount of air through the tube. Then the length of the stain is measured, or the degree of color change is determined from calibration charts. In many tubes operating on the length-of-stain principle, calibration scales reading directly in gas or vapor concentration are printed on the tubes. In some other tubes which can be used with more than one material, lengths of stain are marked in millimeters and concentrations are read from separate charts.

Potential problems in the use of these tubes are the subjectivity in comparing color changes with charts or in determining the true end point of a stain front, and possible interferences from other materials. To avoid subjectivity problems, manufacturers favor length-of-stain techniques over color-degree changes, where possible, and work for packings with finely-grained structures to produce sharp stain fronts. Interferences are often avoided by the use of a pre-cleansing layer in the tubes to selectively absorb interfering components. A fuller discussion of problems and their solutions is contained in Reference 86, pp. S-2 to S-15. Despite some problems of subjectivity and inaccuracy, detector tubes have the strong advantages of simplicity of operation and low cost.

Table 6.3 is a listing of the principal materials detectable by tubes presently being manufactured. This list includes all but six of the gases in the selected list of hazardous materials compiled under this program (Table 4.1), and also

Table 6.3 - List of Materials Detectable by Direct Reading Colorimetric Indicators

Acetaldehyde	Chlorpentafluorethane (Freon 115)
Acetic Acid	Chloropicrin
Acetone	Chloroprene
Acetonitrile	Chlorotrifluoromethane (Freon 13)
Acetylene	Chromate
Acritet (trade name)	Chromic Acid
Acrolein	Copper
Acrylonitrile	Cumene
Aliphates Hydrocarbon	Cyanide Ion
Ammonia	Cyanogen Chloride
Amyl Alcohol	Cyclohexanol
Amyl Mercaptan	Cyclohexane
Aniline	Cyclohexylamine
Arsine	Decaborane
Arsenic	Diborane
Benzene	Dibromoethane (ethylene dibromide)
Benzylbromide	1, 1 Dibromoethane
Benzyl Chloride	Dichlorobenzene (ortho)
Beryllium	Dichlorodifluoromethane (Freon 12)
Bromine	Dichloroethane (ethylene dichloride)
Bromobenzene (mono)	Dichloroethylene
Bromoform	Dichloroethyl Ether
Butadiene	Dichloronitroethane
Butane	Dichloropropane
Butanone (MEK)	Dichlorotetrafluoroethane (Freon 114)
Butyl Acetate	Diethylamine
Butyl Alcohol	Diethylbenzene
Butylamine (n)	Diethyl Ether (ethyl ether)
Butyl Cellosolve	Diethyl Sulfate
Butylene	Dimethyl Acetamide
Butyl Mercaptan	Dimethylamine
Carbon Dioxide	Dimethylaniline
Carbon Disulfide	Dimethyl Ether (methyl ether)
Carbon Monoxide	Dimethylformamide
Carbon Monoxide (in blood)	Dimethylhydrazine (uns) (UDMH)
Carbon Pretube	Dimethylsulfate
Carbon Tetrachloride	Di-n-propylamine
Cellosolve	Dioxane
Chloral Hydrate	2-Ethoxyethanol (cellosolve)
Chloride Ion	Ethyl Acetate
Chlorine	Ethyl Alcohol
Chlorine Dioxide	Ethylamine
Chlorobenzene	Ethyl benzene
Chlorobromomethane	Ethyl Bromide
Chlorodifluoroethane (Genetron 142B)	Ethyl Chloride
Chlorodifluoromethane (Freon 22)	Ethyl Ether (diethyl ether)
Chloroform	Ethylene
Chloroformates	Ethylene Dibromide
Chloronitropropane	Ethylene Dichloride (dichloroethane)

Table 6.3 - List of Materials Detectable by Direct
Reading Colorimetric Indicators (Cont'd.)

Ethylene Imine	Methylamine
Ethylene Oxide	Methyl Bromide
Ethylidene dibromide	Methyl Chloride
Ethyl glycol acetate	Methyl Chloroform (trichloroethane)
Ethyl Mercaptan	2-Methyl Cyclohexanol
N-Ethylmorpholine	Methyl Ethyl Ketone (MEK)
Extraction Solvents	Methyl Ether (dimethyl ether)
Fluorotrichloromethane (Freon 11)	Methyl Chloride (dichloromethane)
Formaldehyde	Methyl Isobutyl Ketone
Formic Acid	Methyl Isobutyl Carbinol (methyl amyl alcohol)
Frigen R11 (trade name)	Methyl Mercaptan
Fumi-1-Gate (trade name)	Monochlorobenzene
Furan	Monomethyl aniline
Furfuryl Alcohol	Monostyrene
Gasoline (see Hydrocarbons)	Nickel
Heptane	Nickel Carbonyl
Hexane	Nitric Acid
Hydrazine	Nitric Oxide
Hydrocarbons	Nitroethane
Hydrogen	Nitrogen Dioxide
Hydrogen Chloride	Nitrogen Oxides
Hydrogen Cyanide	Nitro glycol
Hydrogen Fluoride	Nitromethane
Hydrogen Selenide	Nitropropane
Hydrogen Sulfide	Octane
Insect-0-Fume (trade name)	Olefins
Iron	O-toluidine
Isoamyl Alcohol	Oxidants
Isobutyl Acetate	Oxygen
Isobutyl Alcohol	Ozone (see also oxidants)
Isooctane	Pentaborane
Isopropyl Acetate	Pentane
Isopropyl Alcohol	Perchloroethylene (tetrachloroethylene)
Isopropylamine	Petroleum Hydrocarbons
Kerosine	Phenol
Lead (inorganic)	Phosgene
Lead Tetraethyl	Phosphate
Lead Tetramethyl	Phosphine
Liquid Gas	Propane (see hydrocarbons)
LP Gas	Propyl Acetate
MDI (methylene-bis [4-phenylisocyanate])	Propyl Alcohol
Mercaptan	Propylene
Metasystox (trade name)	Propylene Dichloride
Methacrylonitrile	Propylene Imine
Methane (natural gas)	Propylene Oxide
Methyl Acetate	n-Propyl Mercaptan
Methyl Alcohol	

Table 6.3 - List of Materials Detectable by Direct
Reading Colorimetric Indicators (Cont'd.)

Propyl Nitrate
 Pyridine
 Sec-Amyl Alcohol
 Sec-Butyl Alcohol
 Selenium
 Stibine
 Styrene (monomer)
 Sulfate
 Sulfur Dioxide
 Sulfide Ion
 Systox (trade name)
 Termi-Gas (trade name)
 Termi-Nate (trade name)
 Tert Amyl Alcohol
 Tert Butyl Alcohol
 Tert Butyl mercaptan
 Tetrabromoethane
 Tetrachloroethane
 Tetrachloroethylene
 (Perchloroethylene)
 Tetrachloropropane
 Tetraethyl Lead
 Tetrahydrofuran
 Tethydrothiophene
 Tetramethyl Lead
 Toluene
 Toluene Diisocyanate (TDI)
 Toluene Diisocyanate urea
 Town Gas
 Trichloroethane (methyl chloroform)
 Trichloroethylene
 Trichlorofluoromethane
 Trichloropropane
 Trichlorotrifluoroethane (Freon 113)
 Triethylamine
 Trifluoromonobromomethane (Freon
 13B1)
 Trimethylamine
 Vinyl Acetate
 Vinyl Chloride
 Vinyl Pyridine
 Water Vapor
 Xylene
 Zinc

Ref. 86, pp. S-17 to S-18, with
permission.

includes many of the volatile liquids in Table 4.1. Altogether, 71 out of the 115 materials in Table 4.1 are detectable by some form of detector tube. Allowing for the fact that many of the materials in Table 4.1 are solids or non-volatile liquids, this represents reasonably good coverage. It is emphasized that the detector tubes are designed only for gases, vapors, and mists.

Threshold limits or sensitivities of the tubes vary widely from material to material, depending on the nature of the chemical reaction and the intended use of the tube. Tubes can be specifically designed for high or low concentrations, reaching as low as 0.01 ppm in some cases. Lower limits are typically on the order of one to several ppm, and ranges cover up to the hundreds or thousands of ppm (106).

The principal characteristics of kits produced by the four major manufacturers are summarized in Table 6.4. Prices generally range from about \$75 to \$100 for pump kits, and from \$10 to \$15 for a box of ten or twelve detector tubes, with some of the more exotic tubes running as high as \$25 a box. An illustration of one of the pumps and sets of detector tubes is given in Figure 6.6. As can be seen, the instruments are generally small, light in weight, and suitable for field operation. Kits are typically available with extension hoses for semi-remote operation. The longest standard hose is that made by MSA, 50 feet long. Experimental studies could be made to determine the maximum distance over which one could draw vapors in hazardous material operations, perhaps by increasing the hose diameter.

One additional comment should be made about the MSA kits. A unit called the Universal Testing Kit is available with accessories to allow use of detectors other than the sealed glass-tube-type discussed up to this point. Other types of detectors are tubes freshly filled with relatively unstable chemicals, and chemically impregnated filter papers held in a special adapter. These additional types of detectors allow the kit to be used for a wider variety of materials other than one using sealed glass tubes alone.

Table 6.4 - Detector Tube Kits

	MSA (Ref. 106)	NATIONAL DRAEGER (Ref. 86, pp. S-26 to S-27)	BENDIX/GASTEC (Ref. 86, p. S-21)	MATHESON (Ref. 86, pp. S-28 to S-29)
NUMBER OF MATERIALS DETECTABLE	~140	~110	>113	67
DETECTOR TUBE FEATURES	DIRECT READING (LENGTH READING FOR MULTIPLE- USE TUBES)	MOST TUBES DIRECT READING	DIRECT READING	CONCENTRATION READ ON CALIBRATION CHARTS
PUMP FEATURES	HAND-OPERATED PISTON PUMP	HAND-OPERATED BELLOWS PUMP OR BATTERY-RUN AUTOMATIC PUMP	HAND-OPERATED PISTON PUMP	HAND-OPERATED PISTON PUMP
PUMP WEIGHT		12 OZ (BELLOWS PUMP) (0.34 KG)	10 OZ (0.28 KG)	20 OZ (0.57 KG)
KIT WEIGHT		4 LB (1.8 KG)		5 LB (2.3 KG)
ACCESSORIES	10' (3 M), 25' (7.6 M) AND 50' (15.2 M) EXTENSION HOSES; PYROLYZER; REAGENTS; FILTER PAPERS; SMALL CASE FOR PUMP; OR LARGE METAL CASES FOR PUMP, TUBES, ETC.	3 METER EXTENSION HOSE; METAL CARRYING CASE 5 x 6 1/2" (13.17 CM)	EXTENSION HOSE; HOT PROBE; LEATHER CARRYING CASE	METAL CARRYING CASE

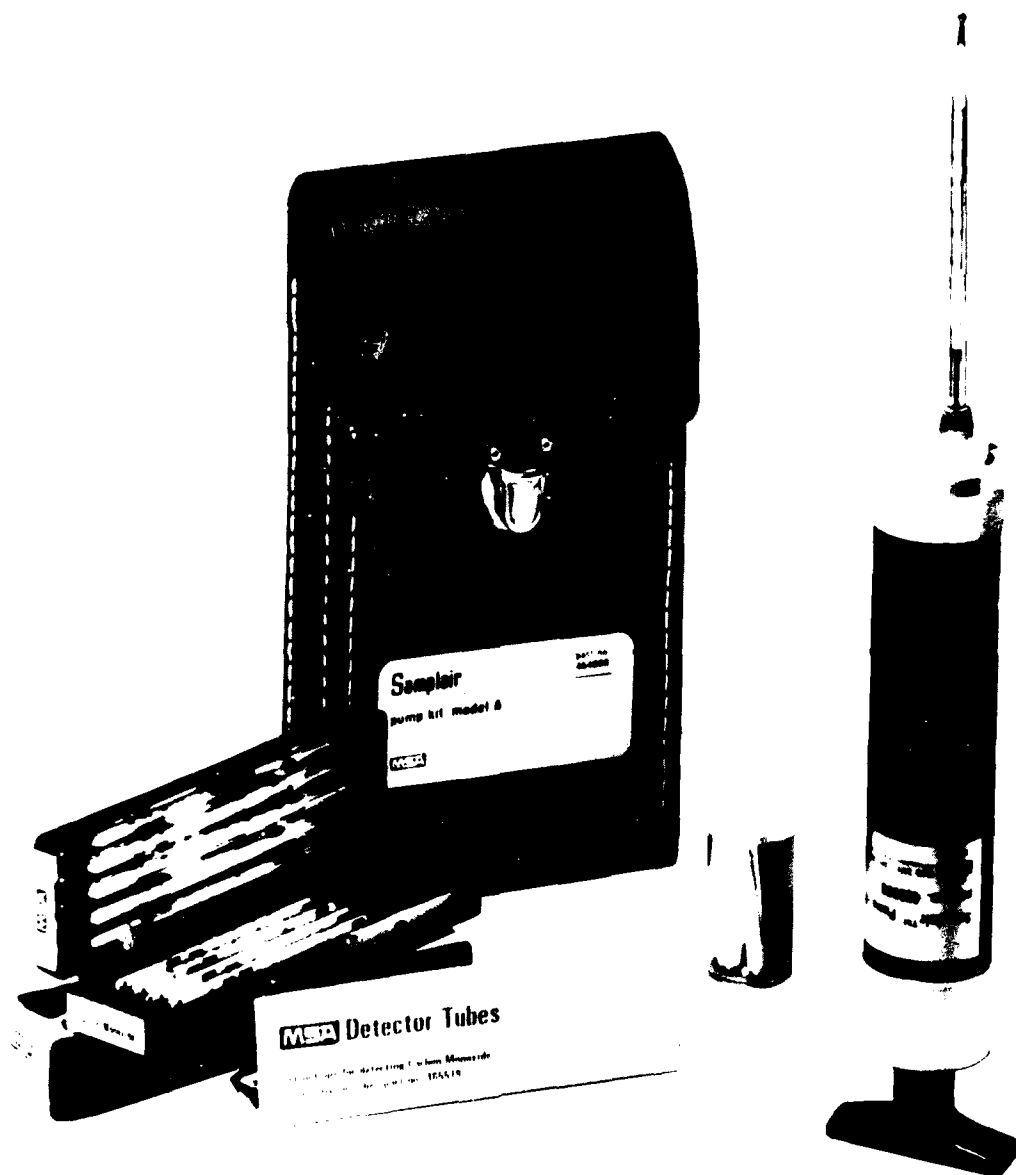


Fig. 6.6 - MSA Samplair Pump, Model A, and Detector Tubes
(Used with permission of Mine Safety Appliances Co.)

The detector tubes discussed in this section have generally been intended for use in industrial or environmental monitoring. When considered from the point of view of hazardous material accident applications, they suffer from the shortcomings common to many of the techniques evaluated in this study; each tube is specific for one material or, at most, a few materials. Hypothetically, if faced with a spill involving an unknown material, one could take a detector tube kit and begin systematically breaking and pumping through tubes in an attempt to find one that would register the unknown. Such a procedure would obviously be tedious and time-consuming. Yet, the procedure would be simple to follow and relatively inexpensive. One could perhaps narrow down the possibilities using sight and smell. Moreover, kits exist which could be put to use now with little adaptation or development. If such a use were envisaged, the possibility of designing detector tubes for hazardous materials not already covered could be investigated.

Beyond identifying an unknown material, there are other situations related to hazardous material accidents where detector tubes could be more useful. In an accident where the identity of the material was suspected, but not known for certain, these tubes could aid in verification. Also, during the course of mitigation and control efforts, once a material had been identified, these tubes would be a simple and inexpensive way to monitor vapor concentrations to aid in evacuation, crowd control, and protection of emergency personnel. With the low cost of the pumps and detector tubes, any moderate-sized fire company should be able to afford a kit. The number and variety of detector tubes kept on hand would depend in part on the chemicals most likely to be encountered--those manufactured or frequently shipped through an area.

Though detector tube kits are a far cry from the optimum instrument one would design for hazardous material operations, they are simple, inexpensive, and represent a technique which could immediately be put to use, without further development, for some monitoring applications.

6.2.5.1.2 Kits for Water Analysis

Several types of kits have been developed for water analysis, in particular, for the analysis of hazardous materials in water. These kits are discussed here both because of their possible use for a hazardous material spill near a body of water, and because some of the techniques may be applicable for a more general purpose instrument system.

The principal research and development in this area has been conducted by a group at the Chemical Systems Laboratory, Aberdeen Proving Ground, headed by Achille Silvestri, in two successive studies sponsored by the EPA Oil and Hazardous Material Spills Branch of the Industrial Environmental Research Laboratory. The kit developed during the first study has since been produced commercially by Hach Chemical Company, along with a variety of other water analysis kits to be discussed briefly later in this section.

The two types of kits developed in the EPA studies are called the Hazardous Materials Detector Kit (107, 108) and the Hazardous Materials Spills Identification Kit (109). The difference between the two kits is basically that the first uses tests of a non-specific nature to analyze for classes of materials (with the exception of spot tests for three specific serious contaminants), whereas the second kit emphasizes identification of specific contaminants.

The contents and tests performed with the two kits are compared in Table 6.5, and photographs of the components are shown in Figures 6.7 and 6.8. As can be seen from the information in the tables and the photographs, each kit contains many components for a variety of tests. Detailed instructions for the tests are given in manuals; however, performance of the tests would require some knowledge of chemical procedures and previous training. The tests, though simple enough to perform in the field, are relatively time-consuming, requiring time to set up the equipment, run the test, and record and analyze the data. Further details of each kit are discussed below.

Table 6.5 - Comparison of Two Chemical Kits

	Hazardous Materials Detector Kit (Refs. 107, 108)	Hazardous Materials Spills Identification Kit (Ref. 109)
Major Components	<p>pH Meter Spectrophotometer Conductivity Meter Filter Assembly Detector Tubes Effervescent Jar & Tablets Enzyme Tickets, Buffer, & Substrate Reagents Beakers & Other Accessories Battery Supply</p>	<p>Inverter/UV Lamp Unit with Low Temperature Hot Plate (Requires 12 V DC Battery e.g., Vehicle Battery) Sample Extraction Apparatus Filter Assembly Detector Tubes Effervescent Jar & Tablets Thin-Layer Chromatography (TLC) components CHEMet Ampoules Spray Reagents & Other Reagents Detector Papers Beakers, Test Tubes & Other Acces- sories Card File Data Retrieval System</p>
Tests Performed	<p>General Assessment: Appearance Color of Filtered Water Color of Suspended Matter Spot tests for Cholinesterase Inhibitors, Benzene, Heavy Metals, Phenol and Cyanide Relative Measurements: pH Conductivity Turbidity Nitrate Nitrogen Color Sulfate Phosphate Ammonia Nitrogen Chloride Fluoride</p>	<p>Detector Paper tests for inorganic compounds CHEMet tests for organics and certain inorganic metal compounds Spray Reagent tests for inorganic metal compounds Spot tests for organic nitro com- pounds, acetaldehyde, and Esters Gutzeit test for Arsenic Detector Tube tests for volatile organics Thin-Layer Chromatography tests for Amines, organic acids, organo- chlorine materials, thiophosphates, and phenol Alcohol tests</p>

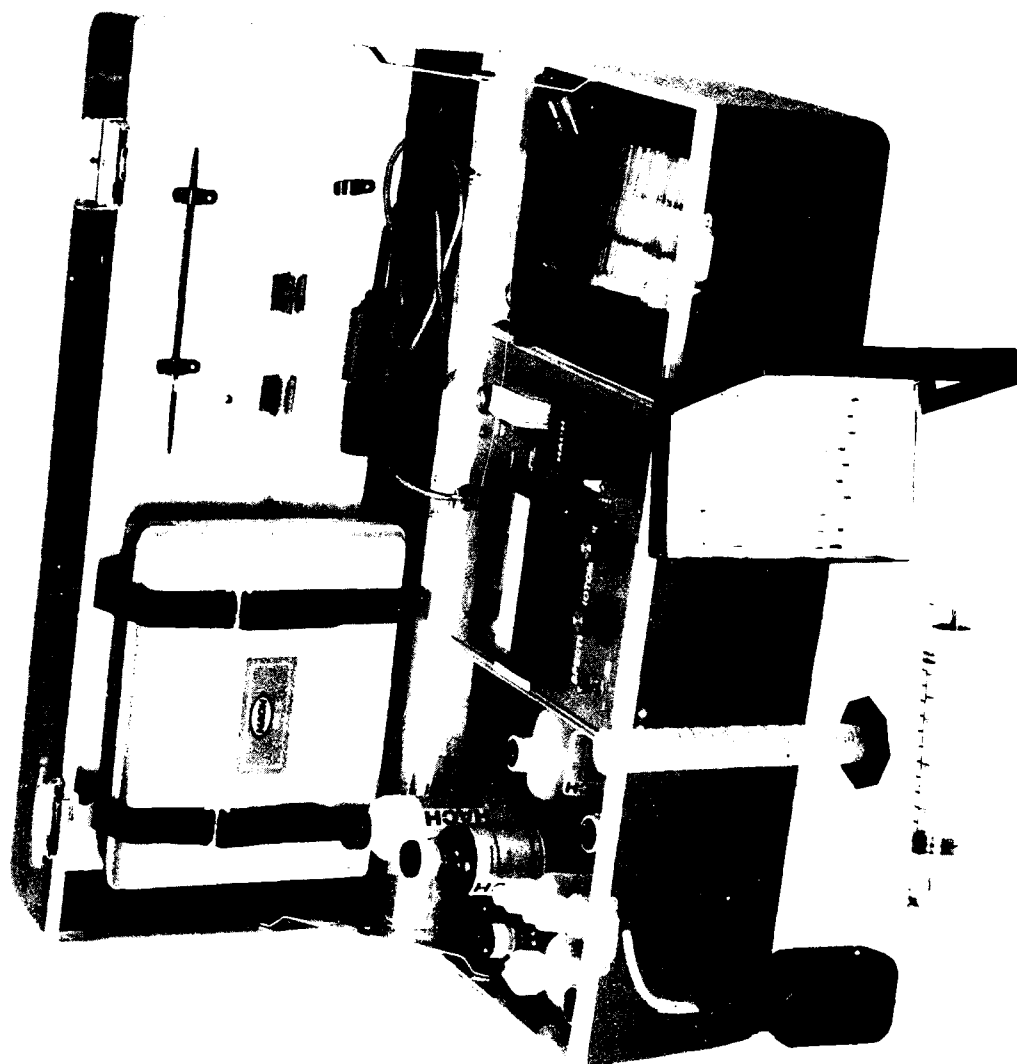


Fig. 6.7 - Hazardous Materials Detector Kit
(Used with permission of Hach Chemical Co.)

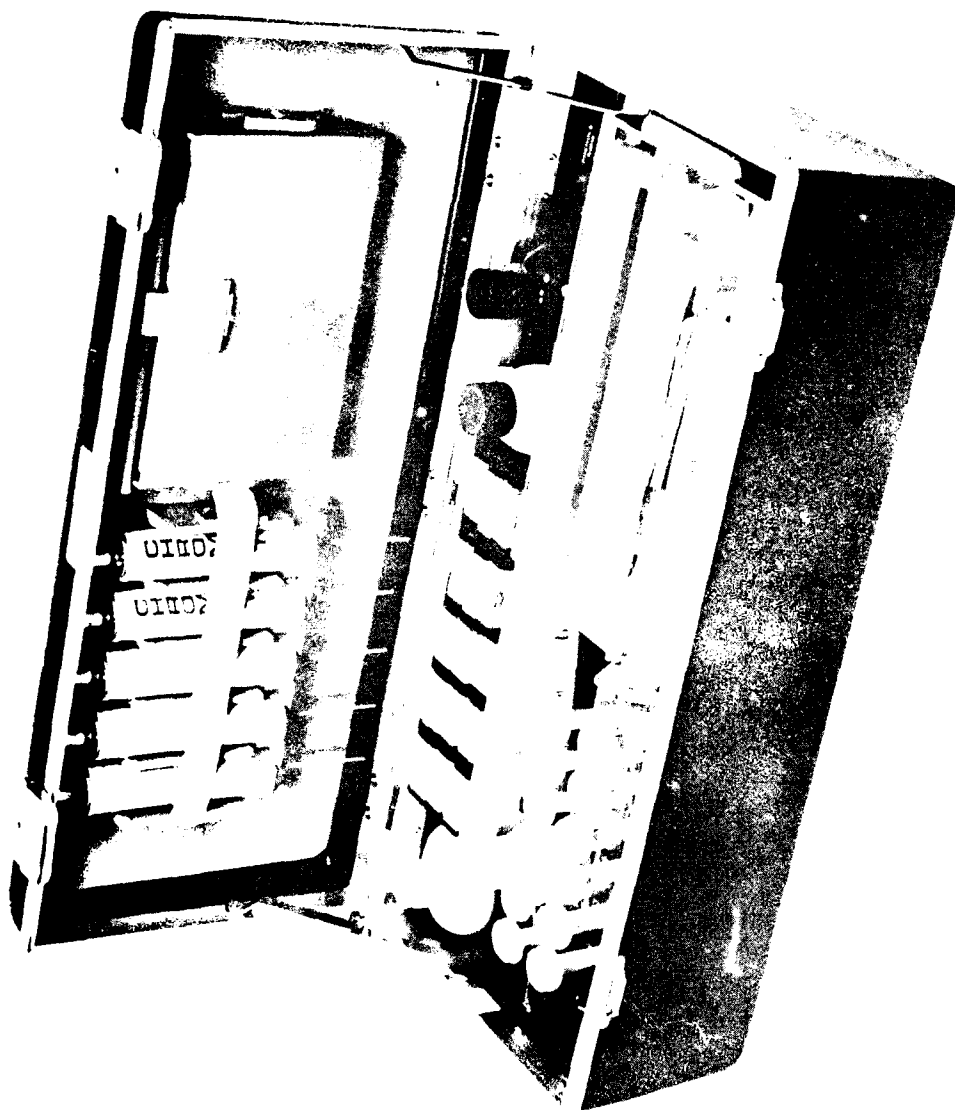


Fig. 6.8a - Hazardous Materials Spills Identification Kit,
Reagents/Auxiliary Equipment Package

(Used with permission of U.S. Army, photograph taken by Henry Bellmeyer)

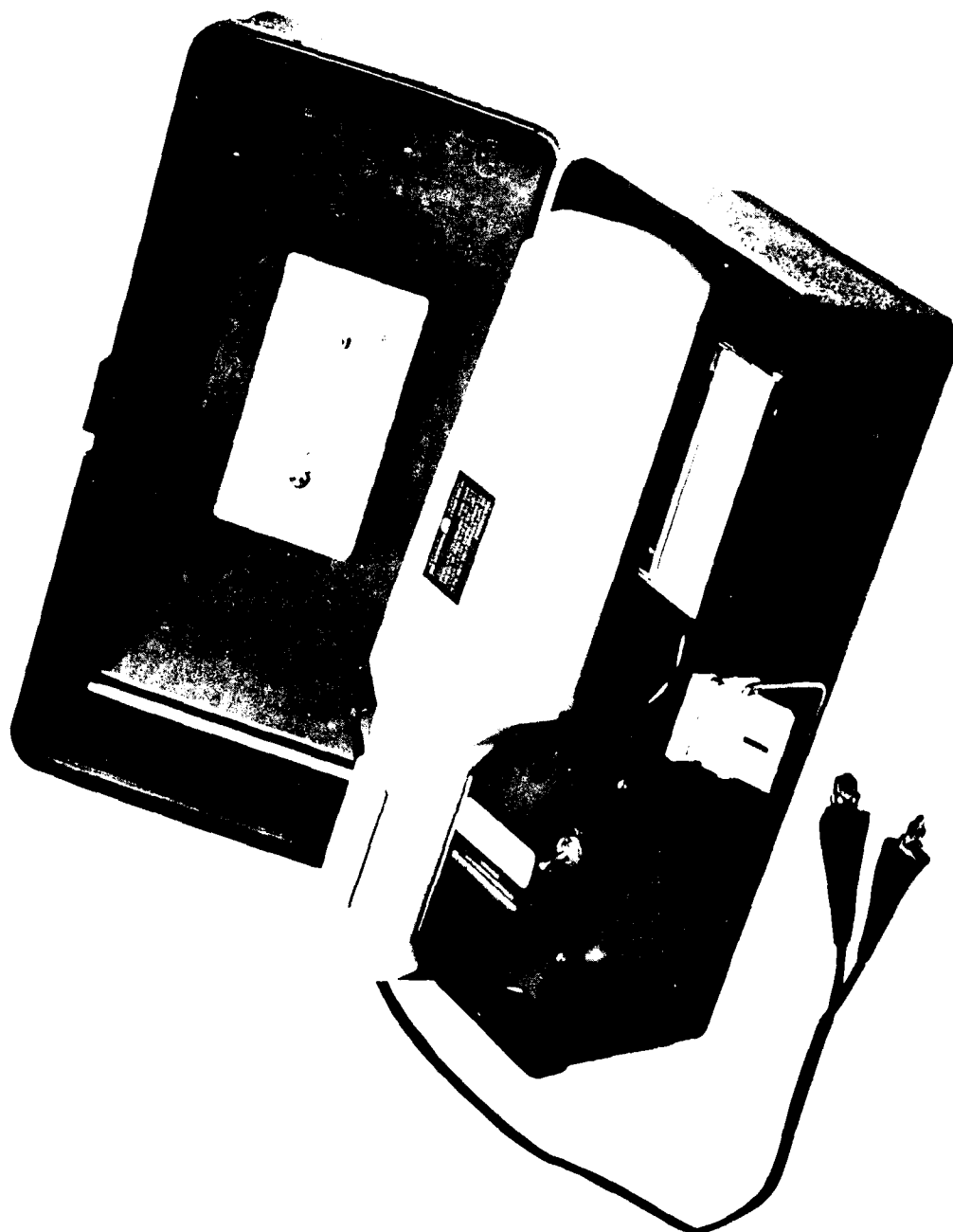


Fig. 6.8b - Hazardous Materials Spills Identification Kit, Inverter/UV Lamp Unit
(Used with permission of U.S. Army, photograph taken by Henry Bellmeyer)

The first kit, the Hazardous Materials Detector Kit (or simply, Detector Kit) was designed to allow an investigator of a spill in inland waterways to determine, for a given area of water, (a) whether that area was contaminated in some way, and (b) what general type of class of contaminant was present. The manual for the kit (107, pp. 52-78) describes a systematic approach involving three groups of tests: General Assessment, Spot Tests, and Relative Measurement Tests. As mentioned, the kit is not designed to identify many specific materials; however, the presence of most of the materials in the Selected List of Hazardous Materials (Table 4.1) would be detectable by use of this kit. Table 6.6 gives more detail on the types of substances detected by the individual tests performed with this kit. As can be seen from the last column of this table, the cumulative time for running all of the tests in the kit would be close to an hour, exclusive of time to set up the kit and analyze the data. Cost of the commercial model of this kit is \$1350.00.

The second kit, the Hazardous Materials Spills Identification Kit (or ID Kit), allows both more specific and more open-ended types of analysis. A significant aspect of this kit is the data card set called the Instant Data System (IDS). These cards contain information on specific materials, information that can be correlated with test results for material identification. A single test may not provide unambiguous identification of a material, but results from several tests can be combined to discriminate one material from another. For example, Malathion produces a light brown stain in a benzene detector tube, a dark brown stain in an acetone detector tube, a white to light gray spot in one type of thin-layer chromatography (TLC) test, and a brown spot in another TLC test (109, p. 62). This combination of reactions could be used to distinguish Malathion from other materials which, for instance, might produce a light brown stain in a benzene tube.

Table 6.6 - Hazardous Materials Detector Kit Parameters
(Ref. 108, used with permission)

Test	Results	Method	Types of Substances Detected	Approximate Minimum Detection Level	Time Per Test Minute
Cholinesterase Inhibitors	Qualitative	Enzyme Ticket	Carbamate and organophosphorus insecticides, chlorosulfonic acid	<3 mg/l	7
Benzene	Qualitative	Detector Tube	Benzene, mono and di-substituted benzenes, naphthalene, isoprene, methyl mercaptan, some sulfides, chlorinated herbicides	1 mg/l	2
Heavy Metals	Qualitative	Extraction/ Test Tube	Cadmium, cobalt, copper, lead, mercury, nickel and zinc compounds	<10 mg/l	1
Phenol	Qualitative	Extraction/ Centrifuge Tube	Substituted phenols, catechol, aromatic alcohols	0.01 mg/l	1
Cyanide	Qualitative	Detector Tube	Cyanide and cyanide compounds, acetone cyanohydrin	0.005 mg/l	1
pH	Quantitative	pH Meter	Organic acids and anhydrides, mineral acids and bases	0.2-14 pH units	1
Conductivity	Quantitative	Conductivity Meter	Inorganic compounds, phosgene, uranyl acetate	0-20,000 μ mhos/cm	1
Nitrate	Quantitative	Spectrophotometric	Acetone cyanohydrin, nitrate compounds, nitrogen dioxide	0.01 mg/l	6
Nitrogen	Quantitative	Spectrophotometric	Chromium, cobalt, copper and nickel compounds, potassium permanganate, azo dyes	5 color units	1
Sulfate	Quantitative	Spectrophotometric	Inorganic sulfates	2.5 mg/l	9
Phosphate	Quantitative	Spectrophotometric	Phosphates and certain phosphorus compounds, arsenates, arsenites and bromides	0.05 mg/l	2
Ammonia	Quantitative	Spectrophotometric	Organic and inorganic ammonia-containing compounds	0.05 mg/l	9
Nitrogen Chloride	Quantitative	Spectrophotometric	Sulfides, bromides, cyanides, thiocyanates, chlorides	5 mg/l	9
Fluoride	Quantitative	Spectrophotometric	Aluminum sulfate, fluoride compounds	0.1 mg/l	2
Turbidity	Quantitative	Spectrophotometric	General appearance	0-500 FTU	1

This second kit is still under evaluation by EPA, and is not produced commercially, although the possibility exists that it will eventually reach commercial status.

One significant aspect of the ID Kit as it relates to general application to hazardous material accidents is that many of the tests can be performed on neat samples, for example, a pile of dry material or a puddle of liquid. Tests can also be performed on contaminated soil samples; procedures are described in the manual for sample separation and preparation. Thus, though this kit was also intended for inland waterway use, its potential applications are broader than those for the Detector Kit. The ID Kit, or some development from it, could be used for those solid or non-volatile liquids which would not be detectable by a remote or non-remote gas and vapor analyzer.

Balancing the versatility of the ID Kit is the fact that its use would require even greater training than the Detector Kit. As the manual for the kit indicates, the skills required to operate the kit are easily learned, but the task of interpreting the data is more challenging (109, p. 50). A certain level of previous experience would contribute toward drawing sound conclusions from the individual bits of information.

As noted above, in addition to manufacturing the Hazardous Materials Detector Kit, the Hach Chemical Company markets a variety of other kits for specialized applications. The types available include a portable environmental (water) lab, an acid mine drainage test kit, a boiler and cooling water test kit, a wastewater analysis kit, and a fish farming test kit. A number of other smaller kits are also available for measuring specific parameters or materials in water, for example, dissolved oxygen or phosphates. Further details on all of these kits are given in Reference 110. One or other of these kits might conceivably be of use for hazardous material emergency applications in particular areas, or by agencies with specific responsibilities, for example, a wastewater treatment plant or

State fish hatchery. However, there is little use for these special-purpose kits for general hazardous material applications.

To summarize the applicability of water analysis kits to hazardous material emergencies, both the Detector Kit and the ID Kit could be useful in communities where hazardous material spills would be likely to contaminate bodies of water. Because they make use of a variety of separate tests and require training, both to perform the tests and to interpret the results, neither kit is seen as a prime candidate for development for first-on-the-scene response. The procedures used in the ID Kit are applicable to neat samples, solids or liquids, and to soils; so this kit has application beyond water analysis. Some further development of a kit aimed specifically at identifying solid and non-volatile liquids could be a useful adjunct to a hazardous gas and vapor analyzer.

6.2.5.1.3 Chemical Agent Detector Kit

One final type of kit which deserves brief discussion for possible application to hazardous material emergencies is the U.S. Army M256 Chemical Agent Detector Kit (111). This kit is intended not to quantify, but to detect the presence or absence of harmful quantities of specific chemical war agents.

The kit, manufactured by Bendix Instruments, consists of a carrying case with 12 identical detector packets. Each packet contains directions and materials for performing 4 simple tests to determine the presence or absence of blood agents, nerve agents, and two types of blister agents in the air. In addition, detector papers are included to test for liquid toxic agents on surfaces. All tests are based on color changes in test spots or on the detector papers. For one test, a detector crayon-button is rubbed on a special tab, and for the other three tests for agents in the atmosphere, small vials contained in plastic pouches are broken to allow the contents to mix onto the detecting test spots. There is even a small heater tab where heat is generated by an exothermic chemical reaction for one test.

Though liquids are used, they are contained in the plastic coverings. The kit is intended to enable a relatively unskilled soldier to test for the presence of toxic agents in the field in a few minutes, without additional tools or equipment.

Though the specific poisons for which this kit was developed are not likely to be encountered in civilian emergencies, the concept of a small, simple, inexpensive self-contained kit is an attractive one. The large number of possible hazardous materials would make the design of a simple kit difficult, if not impossible. Yet, there would be a trade-off between extent of coverage and simplicity. A pilot study could determine the number of materials detectable with a manageable number of simple tests. The kit would thus be envisaged as a packet which an emergency worker could carry to determine simply the presence or absence of a relatively extensive number of toxic substances.

6.2.5.2 Instruments for Detecting Limited Groups of Materials

There exist, for pollution and industrial air-quality monitoring, a host of instrument types designed for one particular material, or for a limited number of materials. For single gaseous species, instruments have been designed to detect, among other materials, oxygen, ozone, H_2S , SO_2 , CO , NO/NO_x , and mercury vapor. Nothing further will be said about these single-component instruments. There exist a number of stationary industrial monitoring instruments which also will not be commented on in detail in this section. Finally, there exist instrument systems, for example excitation fluorescence spectroscopy instruments, which though mobile (e.g., in a trailer or van), are not portable, and which are used for the analysis of certain toxic chemicals or petroleum products in water (112). Beyond noting that such instrumentation systems might be used in later-time on-site analyses of spilled materials, these techniques will not be further considered in this study. This discussion will concentrate on portable instruments designed for certain groups of materials, and which would show at least

some potential for mitigation efforts in hazardous material emergencies. The instrument types can be divided into two groups: hydrocarbon/combustible gas detectors, and detectors for other gases and vapors, not necessarily combustible.

6.2.5.2.1 Hydrocarbon and Combustible Gas Detectors

This group of instruments, often referred to as "sniffers", covers a wide range of sensitivities and applications. Instruments exist for simply giving an audible or visible alarm when certain threshold limits are exceeded, or to measure concentrations in percent by volume or percent L.E.L. (Lower Explosive Limit). Instruments exist for narrow ranges of explosive material types, for example, the alkane family of hydrocarbons, or for a broad range of combustibles. In the following paragraphs, after a brief discussion of the principles of detection, several representative instrument types will be described.

The basic detection method for combustible gases is to burn or combust the gases and to use the products or heat of combustion as an indication of the concentration. Two specific applications of this general approach are flame ionization and catalytic combustion.

In flame ionization, the gas to be detected is introduced into a hydrogen flame burning in air or oxygen. In the combustion process, ions are formed, and are collected by an electrode. The current produced is proportional to the concentration of the gas. A detector of this type responds to all organic compounds but is most sensitive to hydrocarbons. Therefore, flame ionization is often chosen for detectors designed for use only with hydrocarbon vapors. Flame ionization detectors are generally calibrated for methane, and concentrations of other gases must be figured by determining the methane equivalent.

Besides producing ions, the combustion process also produces heat. A thermal combustion detection cell consists of a resistance bridge in which the arms are heated filaments. When a combustible gas is introduced across one filament, its

heat of combustion changes the resistance in the filament, causing an imbalance in the bridge. The degree of imbalance is proportional to the concentration, and is read on a meter with an appropriate scale. In many instruments, detection is enhanced by catalytic reactions of flammable gases with an appropriately selected filament material, often platinum; hence, the name catalytic combustion.

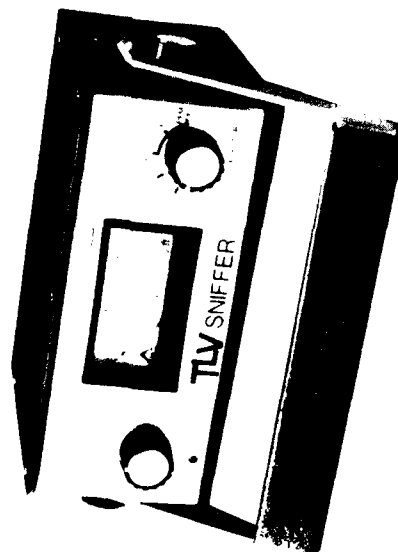
Both flame ionization detectors and catalytic combustion detectors are not entirely specific in the materials to which they respond, though they can be made more or less sensitive to certain groups of materials. For example, combustion detectors can be made to operate at specified filament temperatures so as to ignite the gas of interest (of course, gases igniting at lower temperatures will also respond). Also, the catalyst material can be chosen to favor a desired reaction. Combustion gas detectors are most useful in situations where a known gas or vapor is present, and the desired knowledge is its concentration, in absolute terms, or in terms of Lower Explosive Limit.

Table 6.7 is a comparison of characteristics of several combustible gas detectors. The selection of items in the table is not intended to imply that these detectors are the best of their type. Rather, the intention is to show data for a fairly wide range of types of detectors. Figure 6.9 shows photographs of two different portable detectors.

As can be seen from the table, most of the instruments are quite light and easily portable. Instruments are available in different models designed for specific applications, such as sewer gas monitoring, work around gasoline tanks, or industrial hygiene. Typical prices are \$203 for the MSA Model 2A Explosimeter, without accessories, and \$269 to \$298 for various models of Grace Industries Electronic Nose detectors.

Instruments such as these are already widely used by many fire companies and other emergency groups. For hazardous material emergency applications, their usefulness would not be

Table 6.7 - Characteristics of Combustible Gas Detectors							
Type	Size	Detector Type	Materials	Sensitivity	Reading	Calibration	References
Grace Industries Electronic Nose	Flashlight size	—	wide range of combustible gases	<50 ppm methane	audible or flashing light	Methane	113
Infrared Industries Portable Hydrocarbon analyzer	9 lb. (4.1 kg)	Solid-state	Alkane family of hydrocarbons	25 ppm JP-5	% LEL or ppm	Propane	114
Bacharach TLV Sniffer	5 lb. (2.3 kg)	Catalytic Combustion	wide range of combustible gases	2-3 ppm	ppm	Hexane	Ref. 86 p. U-81; 115
Bacharach Ultra Series	3-3.5 lb. (less batteries) (1.4-1.6 kg)	Catalytic Combustion	wide range of combustible gases	—	% LEL or % nat. gas	Methane	116
MSA Explosimeters & Combustible Gas-Indicators	4-6 lb. (1.8-2.7 kg)	Catalytic Combustion	wide range of combustible gases	<2% Methane	% LEL	Explosimeter: Pentane; Others: up to 5 separate calibrations	117
Scott/Davis Portable Flame Ionization Meter	30 lb. (13.6 kg)	Flame Ionization	Hydrocarbons	<2 ppm Benzene	ppm	Methane	Ref. 86 pp. 9-70 to U-71



6.9a

Bacharach TLV Sniffer



6.9b

Bacharach Ultra I Portable Gas Detector

Fig. 6.9 - Portable Combustible Gas Detectors
(Used with permission of Bacharach/Ambac)

to identify materials, but to monitor for flammable or explosive concentrations of gases or vapors, whether or not the identity of the material were known. For such an application, an instrument with a sensing element responsive to the widest variety of combustible gases would be the most useful.

6.2.5.2.2 Detectors for Other Gases and Vapors

This subsection will briefly discuss a variety of other types of detectors which do not depend on combustion for their principle of operation, and hence are not necessarily limited to combustible gases.

Sunshine Scientific Instruments Co. manufactures an Instantaneous Vapor Detector which operates by UV absorption (86, p. U-134). This instrument is intended primarily for the detection of mercury vapors, which cause strong absorption in the UV region, but it can be used for other vapors with intense enough absorption bands within the spectral range of the UV source. Materials for which detectability is claimed include the following:

acetone	mercury
aniline	naptha
benzene	pyridine
benzyl alcohol	toluene
diethyl acetal	xylene
illuminating gas	

The instrument is portable, at 8 pounds weight, and includes a battery-powered inverter unit.

Two companies manufacture portable halide detectors (halogen compounds are those containing any of the five elements fluorine, chlorine, bromine, iodine, and astatine). The GasTech Halide Detector utilizes the increased UV spectral intensity of an AC spark in the presence of halogens as a detecting principle (86, pp. U-139 to U-140). The Scott/Davis Halide Meter follows a somewhat similar principle, but detects the intensified blue spectral line from a copper electrode in the presence of halide

vapors (86, pp. U-146 to U-147). This instrument is intended specifically for field determinations of halogenated hydrocarbons in air; however, the presence of any halogenated material will cause the instrument to give a reading. Some specific compounds mentioned are carbon tetrachloride, ethyl chloride, methylene chloride, perchloroethylene, and trichloroethylene.

An instrument operating on a principle somewhat similar to flame ionization, but without a flame, is the H-Nu Systems, Inc., Photoionization Analyzer (86, pp. U-162 to U-163). This instrument uses a UV light source that emits photons energetic enough to ionize many air contaminants, particularly organics, but which do not ionize the major components of air. This instrument is specific in that it does not ionize these more strongly bound constituents, but non-specific in that it does not distinguish among the constituents which are ionizable by its UV source. The sensitivity of this 8-pound portable instrument is less than 0.2 ppm for many organics.

Finally, there are two portable continuous colorimetric analyzers manufactured by Pollution Monitors, Inc. (86, p. U-103) and CEA Instruments, Inc. (118). These are wet chemical instruments in which air samples are continuously drawn into the instrument, and trace pollutants are removed from the stream and transferred to a liquid reagent system. The color formation in the reagent is then read by a continuous colorimeter. Both instruments were designed for ambient air monitoring. They can be used for more than one material, but the re-agent must be changed for each different application.

Materials listed as detectable by the CEA instrument are as follows:

acrylonitrile	hydrogen cyanide
ammonia	hydrogen fluoride
bromine	hydrogen sulfide
chlorine	methylhydrazine
fluorine	nitrogen dioxide
formaldehyde	oxides of nitrogen
hydrazine	phosgene
hydrogen chloride	sulphur dioxide

Levels as low as 0.0025 ppm of SO₂ can be detected. Because of the need to interchange reagents, this type of instrument would not be attractive for general-purpose hazardous material use. The fact that it can be used for the symmetrical diatomic molecules bromine, chlorine, and fluorine could make it a candidate as an adjunct to a remote or non-remote IR detector, although the cost, \$4250.00 for the CEA instrument, is high. An instrument of this type might also see use as a continuous monitor during cleanup operations.

The various instruments described in this subsection could find applications in certain aspects of hazardous material emergencies. In geographical areas with a high probability of incidents involving specific groups of materials, for example, halides or mercury-containing materials, specialized detectors could be useful. However, all of the instruments described in this subsection are limited in some way, and do not show promise for development for overall hazardous material detection.

6.2.6 Special-Purpose Instruments

In this section a variety of instrument types which do not fit neatly into previous categories will be briefly commented upon. The instruments to be discussed here generally serve a function other than quantifying the presence of some specific material or group of materials. Those instruments selected for discussion do, however, have at least some potential for application in certain phases of hazardous material emergency operations.

6.2.6.1 Bioluminescent Detectors

In general, the acute toxicity of a material can be determined by testing its effect on some living organism. Determination of toxicity levels according to lethal doses for rats or other laboratory animals is one application of this approach. Water toxicity has been determined using fish or other aquatic organisms. The Beckman Instrument Company has recently incorporated the response of luminescent bacteria to toxic materials into a commercially available instrument.

The Beckman Microtox (119) is an instrument designed to determine acute toxicity in water samples. The instrument does not identify specific toxic materials, but identifies the fact that some material which is biologically harmful is present in a water sample.

In this instrument, a special strain of luminescent bacteria is used as a reagent. Vials containing 2 ml of the bacteria reagent are injected with the water sample to be tested, and toxic concentrations destroy some proportion of the luminescent bacteria. The decrease in luminosity is then measured with a photomultiplier tube and recorded. If a known toxic material is present, the concentration can be determined from calibration curves. Otherwise, the percent decrease in light will determine the general level of toxicity, without reference to the concentration present. In determining degree of toxicity, the implicit assumption is made that the toxic effect on the luminescent bacteria is similar to that on other organisms.

This instrument is relatively fast, with an operation time of about 5 minutes, and by avoiding complicated separation procedures provides a simple method of determining overall water quality. The application to hazardous material accidents is limited, of course, to spills in water, although the possibility of developing such a bioluminescent system to atmospheric analyses could be explored. At present, the cost of the system, \$8700, is high enough that its use in anything but large urban centers is unlikely. Further development and use by agencies other than emergency groups may, however, bring costs down.

6.2.6.2 Alarms and Dosimeters

There are a number of different instruments types, designed for both civilian and military use, for announcing when dangerous levels of certain hazardous materials are reached, or for determining levels of exposure for individual workers.

Portable alarms have been developed for military operations and for field use by civilian workers. Typically, these alarms are specific for single materials or groups of materials.

For example, the U.S. Army M43 Alarm is designed primarily to respond to nerve agents, and to set off a warning sound at concentrations when masking is required (120). The Unico Guardian Combustible Gas Detector/Alarm (86, p. U-96) is intended to detect explosive concentrations of gases or vapors in mines, tunnels, etc. Some of the instruments described in Section 6.2.5.2 which have audible signals could be used as alarms; indeed, the principles on which alarms operate are often similar to those for instruments described in that section.

In hazardous material emergency operations, a very useful application of alarms could be to determine when downwind concentrations from a spill reached dangerous levels. A series of alarms could be placed in a pattern around a spill, particularly in densely-populated urban areas. To be most useful, such alarms would be both responsive to a wide range of materials, and also inexpensive. Since present alarms do not meet these criteria, future development effort in this area would be worthwhile.

Numerous types of personnel monitors have been developed, often for use in industrial environments. Section 6.2.3.2 describes a pocket-sized GC personnel monitor now under development. Other existing types are described briefly below. Some types of personnel monitors act principally as dosimeters; that is, they determine the time-weighted average exposure of workers to specific contaminants. One example is the DuPont Pro-Tek series of badges (121). These are badges designed for specific toxic gases, for example, SO_2 , or for organic vapors. The dose levels are determined after use by readout in a colorimetric or GC unit. While such a badge could be useful to emergency workers, of more value would be a monitor which also serves as an alarm. A series of such alarm monitors is produced by MDA Scientific, Inc. (122). These are pocket-sized units designed to give off an audible alarm when certain threshold limits are exceeded. The monitor units can be incorporated into a microprocessor-based system which records a time-history of levels of exposure. Materials for which these personnel alarm/monitors presently exist are as follows:

ammonia	hydrogen sulfide
aromatic amines	hydrazines
carbon monoxide	nitrogen dioxide
chlorine	organic diisocyanates
dinitrotoluene	phosgene
hydrogen chloride	sulphur dioxide
hydrogen cyanide	toluene diamine

It is emphasized that such monitors are specific for given materials, and that maintaining a system with a complete range of badges or monitors for many materials would be expensive. However, a center in a large city with such a complete capability would be a valuable asset for emergency operations.

6.2.6.3 Leak Detectors

In hazardous material emergencies, some situations will occur in which there is no visible or otherwise obvious rupture in a container, but in which a worker will want to determine if there are any small leaks present. Leak detectors have been developed commercially for a variety of industrial and laboratory applications. Basically, any instrument which can detect small concentrations of materials can serve as a leak detector. A number of the sniffers described in Section 6.2.5.2 are often used for this purpose. Also, various instruments are designated as leak detectors. Some instruments are very specific, for example, the Ion Track Leakmeter designed to detect SF₆ tracer gas in industrial systems (86, pp, U-161 to U-162), whereas others are more general, such as the Gow-Mac Gas Leak Detector (123). For hazardous material applications, a review and possible experimental verification of the ability of existing instruments to detect the widest range of materials would be of value. Where deficiencies were identified, further development of sensing systems could be pursued.

6.2.6.4 Microprobe Analysis

Techniques have been developed for the laboratory analysis and identification of minute quantities of material.

Such techniques could possibly be a useful adjunct to some aspects of hazardous material emergency operations. Examples would be analysis of debris to determine the cause of fires or explosions, analysis of accelerants in arson investigation, or the examination of trace residues on the outside of a container to determine unknown and possibly dangerous contents. Mass spectroscopy and combined GC/MS techniques, already described in Sections 6.2.2 - 6.2.4, are methods that can be used for such analysis. Another recent technique is Raman microprobe analysis.

The principles of Raman microprobe analysis are similar to those described in Section 5.2.1.3 on Raman scattering for remote detection. A sample is irradiated with a single-frequency laser beam, and the frequency (or wavelength) spectrum of the scattered radiation is measured. In the laboratory, the angle at which scattered radiation is measured can be chosen for maximum efficiency.

One advantage of Raman microprobe analysis is that, in addition to elemental identification, molecular structures and/or crystalline structural phases can be determined. Also, the technique is generally non-destructive of the sample being analyzed. Finally, microprobe analysis can be applied to extremely small samples, in the 10-100 picogram range, and for some materials in the subpicogram range (124, p. 69). The equipment used for Raman microprobe analysis is definitely laboratory quality (and size), and this technique would not be considered for development into a portable instrument. The application envisaged would be the collection of samples at a site, with shipment to a lab for later analysis.

A group at the National Bureau of Standards under Edgar S. Etz has pioneered in the development of this technique. References 124 through 127 give details on the specific applications of Raman microprobe analysis. These applications include studies of airborne dust and pollution particles, of trace toxic organic substances in water, and of thin sections of biological tissues for pathological and forensic analysis.

This technique would be applicable to the analysis of causes of hazardous material incidents, or to any situation where identification based on very small quantities of material is required. Possible applications beyond hazardous materials could range from crime investigation, for example, the identification of trace amounts of gunpowder, to the identification of small samples of narcotics.

6.2.6.5 Remote-Controlled Vehicles

While a remote-controlled vehicle could hardly be considered an instrument, the use of such a vehicle as an instrument platform, or as means for obtaining samples remotely, is a possibility. At least one known program is underway to develop such a vehicle.

Developmental Sciences, Inc., of Industry, California, in cooperation with the Oxnard, California, Fire Department, under a grant from the EPA, is working on a Pre-Prototype remotely-controlled vehicle for hazardous material emergencies (128). The intent of the vehicle is to conduct close-up reconnaissance of a spill and transmit information back to a command center, e.g., via a TV camera, and to perform control or mitigation actions remotely. While instrumentation for material identification is not part of the present program, once a vehicle was designed and built, its payload could be modified for various applications.

The projected design configuration is a hovercraft, to enable the vehicle to move over rough terrain and obstacles. The vehicle would be relatively small, with a weight of about 250 pounds. According to the information available for this report, the program is still in its early stages, with no experimental results available. A rough projection of the cost of such a vehicle in production quantities of 500 is \$30,000 per vehicle (128,p. 360).

Though other methods of identifying materials or obtaining samples may be more straightforward, if a vehicle of this type were developed to the production stage, the possibility

of using it also for a material sampling/identification role would be attractive. Therefore, this program should be monitored as it progresses for applications to overall hazardous material emergency operations.

6.2.7 The Human Senses

A few words should be said somewhere in this report about the application of human senses in detecting and identifying hazardous materials. Strictly speaking, the human nose might be considered a non-remote sensor, whereas the eyes would be remote instruments, sensitive to electromagnetic radiation in the visible range.

Human senses cannot be relied on exclusively for the role of detection and identification - some toxic materials give no advance warning to sight or smell. Yet, it would be unwise to neglect a consideration of the contribution that human senses can make to material identification. Many gases and vapors have distinct odors and distinct colors. The human eye is efficient at very long distances (in clear weather) and the human nose can be sensitive in the below ppm range. As noted in Section 5.4.4, some materials, chlorine for example, present a detectable odor well before dangerous levels are reached. Some firemen claim that their sense of smell quickly becomes deadened; however, one could expect it to be more acute at least at the initial encounter with a gas or vapor.

We can quickly recognize the smell of many materials with which we are familiar, gasoline or an orange being peeled, for example. We are able to make subtle distinctions between similar odors - an orange and a tangerine. But we would be unable to identify a material with which we were unfamiliar, even if it had a distinctive odor. Many people will not be able to recognize ozone unless they have worked in an electrical lab. Few people would recognize acrolein or phosgene, though these substances have distinct odors. This suggests that a training program in smell and sight identification would be a valuable asset for emergency workers.

The purpose of such a training program would be to familiarize emergency workers with the physical characteristics of hazardous materials likely to be encountered in their missions. Attendees would be exposed to safe quantities of gases and vapors in order to learn by experience their characteristic odors. Materials (gases, liquids, and solids) that have distinct visible characteristics would be viewed and studied. Characteristics would include color, shape and size of crystals, viscosity of liquids, and fuming or vapor cloud characteristics.

Though senses other than smell and sight are less important, they should not be ignored. Taste works closely with our sense of smell. Our ears can hear the hissing of a leak or crackling of an electrical discharge, and our sense of touch can aid in detecting temperature changes, motions, textures, etc.

Thus, with the emphasis of this study on instrumentation, the importance of the human senses should not be neglected. Particularly, in the area of gaining familiarity with smells and visible signs, the senses can make an important contribution to hazardous material detection and identification.

6.3 Summary of Non-Remote Systems

In this section, some of the pertinent details of the instrument systems which depend on sampling a material are summarized. No attempt is made in this section to identify specific models; this information is contained in the preceding portions of Section 6.0. Table 6.8 lists the features which are applicable to a consideration of these instrument types for hazardous material emergency use. The information in the table oversimplifies in many instances since there are different versions of certain instruments; however, the table allows comparison of one instrument type with another.

Of the many instrument types listed in Table 6.8, the two which show some promise for application to the difficult task of identifying an unknown material in the field, from a large number of possibilities, are a Dispersive IR Absorption instrument and a portable Gas Chromatograph/Mass Spectrometer. Of

Table 6.8 - Summary of Non-Remote Systems

TYPE OF SYSTEM	REFERENCE SUBSECTION	PRODUCTION STATUS	PORTABLE VERSION	MULTI-MATERIAL CAPABILITY	APPLICATION TO GENERAL HAZARDOUS MATERIAL I.D.	OTHER HAZARDOUS MATERIAL EMERGENCY APPLICATION
NDIR Absorption	6.2.1.1	Commercially available	yes	no	no	little
Discrete Frequency Absorption	6.2.1.1.1	Lab-type	no	no	no	little
Dispersive Absorption	6.2.1.2	Commercially available but without hazardous material discriminator	yes	yes	yes	Monitor concentration once I.D. is known.
Gas Chromatography or GC/MS combination	6.2.3	Commercially available	yes	Yes, but variety of columns needed	Limited in that I.D. function must be performed separately	Use to separate components in complex mixtures.
Mass Spectroscopy	6.2.2 & 6.2.4	Developmental status	yes	yes	yes	Monitor concentrations; aid in cleanup.
Detector Tubes	6.2.5.1.1	Commercially available	yes	Yes, if kit with many tubes is used	limited	Verify I.D.; monitor concentrations.
Water Analysis Kits	6.2.5.1.2	Some types are commercially available	yes	yes	limited: time-consuming	Analyze spills in water or soil; neat samples of solids or non-volatile liquids.
Chemical Agent Kits	6.2.5.1.3	Produced for military for some materials	yes	Limited number of materials	no	Detect general presence or absence of some hazardous material.
Combustible Gas Detectors	6.2.5.2.1	Commercially available	yes	Limited groups of materials	no	Monitor explosive or flammable concentrations of gases.
Detectors for Groups of Gases	6.2.5.2.2	Commercially available	yes	Limited groups of materials	no	Monitor presence of groups or identify certain specific materials.

Table 6.8 - Summary of Non-Remote Systems (Cont'd.)						
TYPE OF SYSTEM	REFERENCE SUBSECTION	PRODUCTION STATUS	PORTABLE VERSION	MULTI-MATERIAL CAPABILITY	APPLICATION TO GENERAL HAZARDOUS MATERIAL I.D.	OTHER HAZARDOUS MATERIAL EMERGENCY APPLICATION
Bioluminescence	6.2.6.1	Commercially available	yes	Yes, but does not identify material	no	Determine presence of toxic materials in water.
Field Alarms	6.2.6.2	Commercially available	yes	Limited number; does not identify material.	no	Monitor spread of vapor cloud or plume
Personnel Dosimeters/Alarms	6.2.6.2	Commercially available	yes	Specific units for specific materials	no	Monitor individual exposure to a hazardous material.
Leak Detectors	6.2.6.3	Commercially available	yes	Limited groups; does not identify material	no	Identify leaks not visibly apparent
Raman Microprobe Analysis	6.2.6.4	Lab-type	no	yes	no	Identify small quantities of material after the fact.
Remote Controlled Vehicle	6.2.6.5	Developmental Status	mobile	---	---	Serve as platform for instrument or sampling system.
Human Senses	6.2.7	---	yes	Limited number of materials	limited	Serve as a supplement to instrument use through proper training.

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LOCUS INC STATE COLLEGE PA
INSTRUMENTATION FOR DETECTING HAZARDOUS MATERIALS. (U)
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these two types, the Dispersive IR instrument exists commercially, but not in a form which allows complete discrimination of many materials. A program to develop this instrument for the specific hazardous material emergency mission would seem highly desirable. The GC/MS instrument is in a developmental stage for a configuration suited to hazardous material emergencies. This effort should be closely monitored, and perhaps supported to some extent by FEMA.

Other instruments with a more limited application to the general hazardous material identification task are detector tubes and certain forms of chemical kits. Detector tubes are attractive because they are simple, inexpensive, and available now. Their application to identifying an unknown would be inefficient, but they would have other ancillary uses in hazardous material emergencies. Chemical kits are relatively cumbersome and time-consuming. One particularly attractive feature, however, would be their ability to identify solids and non-volatile liquids, as well as contaminated waters and soils, functions which a remote detector or instrument designed for gases and vapors could not perform.

There remain a variety of instruments which could be useful in some phases of hazardous material emergency operations other than the immediate identification role. The number of such instruments which a given fire company or city might attempt to acquire and employ would depend on its size, funding, the frequency of hazardous material incidents in the community, and factors such as the existence of nearby water transportation routes or of companies dealing with particular classes of materials.

Of general usefulness would be alarms, personnel dosimeters, leak detectors, and combustible gas detectors, which would also serve to identify certain types of leaks. For more special purpose application, depending on location, there are instruments for water analysis, such as bioluminescent detectors or chemical kits, or instruments for limited classes of materials, such as mercury vapors or halides. Most of these instrument types can

profit by some further development effort, either for an increase in the number of materials to which they are applicable, or for increased portability, or reductions in cost.

Finally, with the emphasis on instruments to do certain jobs, the capabilities of the human senses should not be overlooked. Through proper training, emergency workers can learn to recognize the physical manifestations of certain materials, their odors, colors, or textures. Though the human senses are not substitutes for instrumentation, they can aid both in the role of material identification and in the efficient and intelligent use of existing instruments.

7.0 REMOTE DETECTION OF HEAT SOURCES

7.1 Introduction

The remote detection of heat sources by detecting differences in the levels of electromagnetic radiation between the source and its surroundings is a technique that has been exploited for various applications. Wide band radiation, not spectral differences, is sensed. The technique relies on the fact that all objects radiate energy at a rate proportional to their absolute temperature: the higher the temperature, the greater the radiation rate. The phenomenon has been used to derive imagery without need for illumination, to remotely measure effective temperature, to detect the presence of intruders, and for many other purposes.

7.2 Spectral Characteristics

The spectral range of the electromagnetic energy, commonly called thermal emission, extends over the wavelength range from low frequency radio waves through the short waves and microwaves, the infrared, visible and ultraviolet light regions, and on into the x-ray spectrum. Total radiated power is proportional to the fourth power of the absolute temperature of the source.

The distribution of the power over the broad spectrum of wavelengths is also a function of the source's absolute temperature. This relationship, which will be discussed in Section 7.3, follows a more complex function of temperature than does the total radiation. For a given source temperature, the radiation distribution peaks at a distinctive wavelength. As the temperature increases, this peak moves toward the shorter wavelengths. As an example, the radiation peak for a source at 500° Kelvin (440°F) falls at about 6 micrometers, right in the middle of the infrared spectrum.

Transmission characteristics of the atmosphere vary over the entire electromagnetic spectrum. Certain wavelength regions are subject to high attenuation - these bands are found both in the microwave and the infrared regions, but can be avoided by a judicious choice of the operating spectral region for a detection system.

Transmission characteristics of solid substances also vary with wavelength. As is well known, metals are opaque at all wavelengths longer than x-rays. Non-metallic solids exhibit some level of transparency to microwaves, but are, for practical purposes, opaque at the infrared wavelengths.

In a hazardous material emergency, the ability to penetrate solid substances in detecting hot spots is felt to be relatively unimportant since any generation of heat as a result of the emergency situation is almost certain to manifest itself as a temperature rise at the surface of the object or material. Atmospheric transmission factors do require consideration, but at the short detection distances that will typically be encountered, these are not of great consequence.

7.3 Choice of Spectral Range

The choice of spectral range for a simple hot-spot detection instrument depends much more heavily upon the level of radiant energy available than upon transmission vagaries of the atmosphere. A simple comparison vividly illustrates that fact. Comparing Spectral Radiant Emittance for two spectral intervals, one centered at 10 micrometers (IR) and one centered at 1 centimeter (microwaves), we use Planck's Equation:

$$W_{\lambda} = C_1 \lambda^{-5} \left[\exp \left(\frac{C_2}{\lambda T} \right) - 1 \right]^{-1} \quad (7.1)$$

where: W_{λ} = radiant flux per unit area per unit increment of wavelength - Watts/cm²/cm

λ = wavelength - cm

C_1 = 3.74×10^{-12} Watt cm²

C_2 = 1.44 cm deg K

K = temperature - deg K

The above equation assumes a black-body radiating surface. Assume now that we have a black-body source at 500°K (approximately 440°F).

In the microwave region we have:

$$W_{\lambda} = 3.74 \times 10^{-12} \times 1^{-5} \left[\exp \left(\frac{1.44}{1 \times 500} \right) - 1 \right]^{-1} \quad (7.2)$$

whereas in the IR region, we have:

$$W_{\lambda} = 3.74 \times 10^{-12} \times (10^{-3})^{-5} \left[\exp \left(\frac{1.44}{10^{-3} \times 500} \right) - 1 \right]^{-1} \quad (7.3)$$

Although the value of W_{λ} is a function of wavelength, we can compare spectral ranges by assuming it is constant over a small wavelength interval. Considering in each case an increment of 10% of the center wavelength (1 micrometer in the IR, and 0.1 centimeter in the microwave regions), for microwaves the radiant power density, P , is:

$$P = W_{\lambda} \times 0.1 \text{ cm} = 1.297 \times 10^{-10} \text{ Watts/cm}^2 \quad (7.4)$$

for the infrared:

$$P = W_{\lambda} \times 10^{-4} \text{ cm} = 2.22 \times 10^{-2} \text{ Watts/cm}^2. \quad (7.5)$$

Although the above calculations are not rigorous, they demonstrate vividly the huge difference in radiant energy emitted in the two spectral ranges. The practical consequences are that a simple infrared system can provide satisfactory performance, whereas, use of the microwave region requires a highly-sensitive receiving system.

7.4 Available Instruments

7.4.1 Pre-prototype Hand-held Fire Detector

The simplest instrument available is the Pre-prototype Hand-held Fire Detector, Figure 7.1, that was developed for the Office of Civil Defense in the mid-1960's by HRB-Singer, Inc. This unit is simple to use, inexpensive, and reliable. It was



Fig. 7.1 - Pre-Prototype Hand-Held Fire Detector

designed to respond only to a source at temperature differences that will indicate the presence of combustion. If desirable, its thermal sensitivity could be improved. Higher sensitivities have, in fact, been achieved in commercial instruments, as indicated in the next section.

An evaluation of the Pre-prototype system, through trial use by a municipal fire company, was described in the Final Report (129) on the development contract. The results of that trial were deemed to be favorable. The trial evaluation compared two physical embodiments of the same infrared device; one in the shape of an ordinary flashlight, the other having a pistol grip. Firemen who participated in the test indicated a preference for the pistol-grip version, citing such advantages as ease in directing the device toward suspected hot spots.

7.4.2 Commercial Instruments

A device, obviously almost identical in principle to the Pre-prototype system, is advertised by Dyn-Optics, Inc. of Laguna Niguel, California (130). Whereas the Pre-prototype employs a pistol-grip in the favored configuration, the Fire Finder is shaped like an ordinary flashlight. Specifications for this unit are similar to those for the Pre-prototype unit.

Other commercially available heat detectors are the Heat Scanner, manufactured by 3M (131) and a Hand Held Hot Spotter made by Macer Industries (132, pp. 36-7). Both of these instruments have pistol grips. The Heat Scanner has sensitivity settings of low, medium, and high, and advertises that temperature differences as small as 2°F can be detected in the high sensitivity range.

7.4.3 Infrared Thermometers

Several firms advertise a series of hand-held radiation thermometers (133). Figure 7.2 is a photograph of one model of such an instrument. These units are pistol-grip, hand-held devices which determine the radiation temperature of an area covered by the optical field-of-view, and display it on a visual meter. Their utility as an aid to a fireman in a burning building

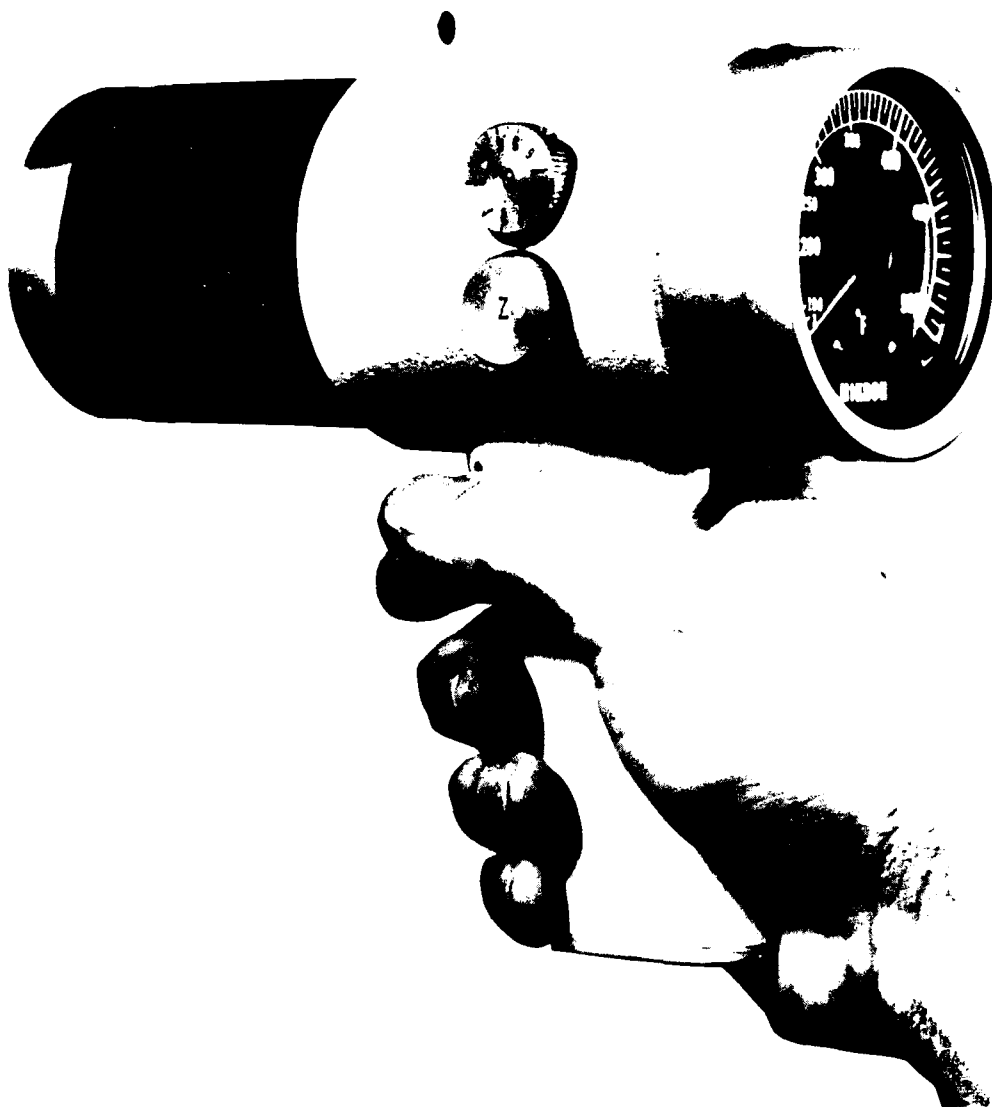


Fig. 7.2 - MIKRON 5 Infrared Thermometer
(Illustration provided by Mikron Instrument Co.)

would be marginal, primarily because of a visual as opposed to an aural output indication. For use as a tool in hazardous material incidents, the visual indicator probably would not represent a serious shortcoming.

7.4.4 Thermal Imaging Devices

A thermal imaging device presents to the viewer a two-dimensional pictorial representation of temperature distribution in the scene observed. The picture obtained is similar to a television picture, but usually at somewhat reduced spatial resolution. Warmer objects show up as brighter objects in the display. No external light is needed for use, so they are equally useful night or day, although a filter may be desirable for daytime use to reduce the effects of solar energy reflection. Two commercial devices are discussed in Subsection 7.4.5.3.

7.4.5 Observations on Infrared Instruments

7.4.5.1 Hot-spot Detectors

The Pre-prototype unit, the Fire Finder, and other commercial units are believed to use basically the same infrared detection technology.

While the Fire Finder does not utilize the preferred pistol-grip configuration, it does have other features that the Pre-prototype does not have. One of the additional features is the inclusion of a self-test feature which would enhance user confidence. Another feature is the apparent use of an audible indicator that does not utilize an ear plug. In our opinion, the use of the ear-plug in the Pre-prototype is a definite disadvantage from the standpoint of operational use.

The Heat Scanner and Hand Held Hot Spotter, as noted, both have pistol grips. These two units have both audible and visual indicators. Thus, if vision is impaired by smoke, the audible signal could be heard, or if ambient noise obscures the sound, the visual indicators can be used.

The advertised cost of the Fire Finder, \$520.00 each, may seem high when considering the apparent simplicity of the

device, but it is probably determined by an intent to amortize development costs over a relatively small sales volume. The Heat Scanner is in the same range at approximately \$500, whereas the Macer unit is less expensive at about \$250 (1978 price). Wide acceptance of these devices could possibly result in decreased unit costs.

7.4.5.2 Radiation Thermometers

The Infrared Thermometers, exemplified by the MIKRON product, Figure 7.2, are quantitative indicators of radiation temperature. It is important to note that the indication presented by this instrument may not be the true temperature of the source. That is due to the fact that the instrument responds to the radiated power density which is a function, not only of the source temperature, but also of a surface property known as emissivity. The Infrared Thermometers have a manual adjustment for inserting an emissivity value. Accuracy of the indicated temperature is, of course, affected by the accuracy of the emissivity value inserted. For detecting relative temperature differences, however, the emissivity accuracy is probably of second order importance.

The Infrared Thermometers have a temperature sensitivity many times greater than that of the Fire Finder and the Pre-prototype Fire Detector. This could be an advantage in some accident situations and a disadvantage in others. For finding combustion areas hidden by smoke, etc., high temperature sensitivity is a disadvantage due to the fact that the instrument will be driven into saturation by high temperatures.

7.4.5.3 Imaging Devices

Most infrared imaging devices are very expensive and have been designed primarily for military use. One non-military system, however, the AGA Thermovision (132, pp. 40-41) has been available for many years. Recently a simplified, hand-held thermal imager, the PROBE EYE has been developed by Hughes Aircraft Corporation (134).

7.4.5.3.1 AGA Thermovision

The Thermovision system is a semi-laboratory type design that is composed of two units; a camera unit and a display unit.

While its thermal and spatial resolution characteristics are moderate to good, it has many disadvantages for field use. It is relatively bulky, heavy, and requires a supply of liquid nitrogen which is used as a detector coolant. The manufacturer claims the camera unit can be hand-held, but the display is roughly the size of a laboratory oscilloscope. Cost of the system is approximately \$60,000 according to Reference 132.

7.4.5.3.2 Probe Eye

The Probe Eye Infrared Viewer is a self-contained, hand-held device, slightly larger than a home motion picture camera. Its performance characteristics are comparable to those of the Thermovision, but the display is viewed through an eyepiece at the rear of the unit. It is small and light enough to be easily hand held.

The Probe Eye uses pressurized argon gas as the detector coolant. The coolant is stored in a small cylinder within the viewer, and one cylinder contains enough coolant for about four hours of continuous operation. An accessory argon booster system is required to re-fill the cylinders.

Since the coolant is stored in gaseous form, it does not represent the degree of inconvenience that the Thermovision liquid nitrogen requirement does, but must still be considered a pertinent factor for field use application.

The Probe Eye, with required accessories, markets for approximately \$10,000.

7.5 Microwave Fire Detectors

At least one company, International Microwave Corporation, has built and publicized a prototype microwave fire detector(135). Its estimated cost is approximately \$3500 per unit.

The major advantage claimed for this unit is its ability to penetrate many obstructions which infrared wavelengths cannot penetrate. Cited are materials such as dense smoke, flame, ash, wood, plastics, fabrics, paper, asbestos, fiberglass, roofing tar, plaster, etc. Actually, smoke and flame do not appreciably affect infrared transmission, but the rest of those listed do.

The prototype microwave unit is approximately a cubic foot in size and weighs about 20 pounds. These parameters could probably be reduced by careful design, but could not easily be reduced to those readily achievable for an infrared device.

It is felt that the microwave technique has little advantage to offer as a hazardous-material accident tool, while exhibiting disadvantages in size, weight, and unit cost.

7.6 Future Development of Hot-spot Detectors

The need for a hot-spot detector as a hazardous material accident tool is considered to be a secondary factor compared to the need for hazardous material-type identification equipment. Imaging devices may have specific applications, such as locating bodies of unconscious victims in smoke-filled rooms. Their high cost, however, would seem to preclude widespread use. But one can postulate situations where a simple, reliable hot-spot detector would be advantageous to have.

The simple devices described earlier (the Pre-prototype Fire Detector and the various commercially produced instruments) are felt to be entirely adequate for quick, reliable hot-spot detection. Furthermore, the hand-held Infrared Thermometers are readily available in case a requirement for their thermal sensitivity should become evident in the future. There appears to be no need, therefore, for any effort at further development of this sort of instrument.

8.0 CONCLUSIONS AND RECOMMENDATIONS

Because detailed conclusions are reached in the preceding sections on materials (Section 4) and on various instrument types (Sections 5, 6, and 7), the restatement of major conclusions and recommendations in this section will be brief. One aspect which has not been given systematic attention in the preceding sections is instrument deployment and training in its use, should an instrument system of a given type be developed to the stage of being ready for field use. A brief discussion of considerations relating to deployment and training (without reference to any particular instrument) is given below, followed by a summary of conclusions and recommendations for specific instrument types.

8.1 Hardware Deployment and Training in its Use

During times of emergency, the number and complexity of problems creates the need for a continuous study of what is happening. Without correct information, an accurate assessment of the situation is not possible. When reliable information is received and proper analysis of that information is made, appropriate responsive actions can be inaugurated.

For emergency operations to be effective, Emergency Management (Civil Defense) organizations at all levels must be prepared to quickly and accurately collect, study, and combine essential information to form a total emergency "Big Picture". This function is performed by the Situation Analysis Group within the Emergency Operating Center (EOC), and permits the most efficient use of available resources.

Of the other groups operating within the EOC, the State and local Police and Fire and Rescue groups are the ones most likely to have direct initial contact at the scene of an incident involving hazardous substances. These incidents may be isolated, such as a vehicle accident, or may be part of an overall major emergency such as a flood, tornado, or even enemy attack. Whatever the case may be, it is imperative that these groups possess the capability to quickly detect and identify any substances that may be hazardous to the population. This is so

during the course of their day-to-day operations as well as in extreme emergency situations.

Each state, county, and local EOC should be equipped with at least one portable unit, when and if such units are developed. This could serve as a back-up to the regular field units if the need would arise where none is immediately available, or as a replacement if a field unit should become inoperable. In addition, depending on populations and relative frequencies of hazardous material incidents, local, county or state centers should be equipped with mobile labs for more sophisticated material analysis in the intermediate, as opposed to immediate, time frame.

Public fallout shelters already have included as part of their standard equipment a detector for monitoring radioactivity. A portable device for detecting the presence of hazardous materials should also be included in the shelter kit. This would add one more dimension to the effort to protect the lives of those within the shelter.

National Guard units are often placed on active duty to assist in times of emergency. During these times, they are performing the same duties as the day-to-day agencies and should possess the same capabilities as their civilian counterparts. This would indicate that a hazardous materials detector should be included as part of their emergency equipment.

Military installations, including naval vessels, have the same general problems that exist in small communities. Therefore, they should also be equipped for quick, accurate identification of hazardous materials. This includes Military Police, Shore Patrol, and military fire and rescue units.

Environmental Protection Agency (EPA) investigators trying to make accurate determinations at leaks, spills, or dump sites are presently stymied by the lack of efficient, reliable detection and identification methods. Extensive EPA research efforts are ongoing, and some of the instrumentation techniques developed are referenced in earlier sections. Portable equipment, especially that designed for water analysis, would greatly expedite their efforts.

Large transportation terminals such as freight yards, airports, and shipping ports where they have their own guard force and fire units may have the need for utilizing portable detection and identification devices. This may be so in the event of accidents in storage, loading, unloading, or in-port transportation of hazardous materials which may not be properly identified.

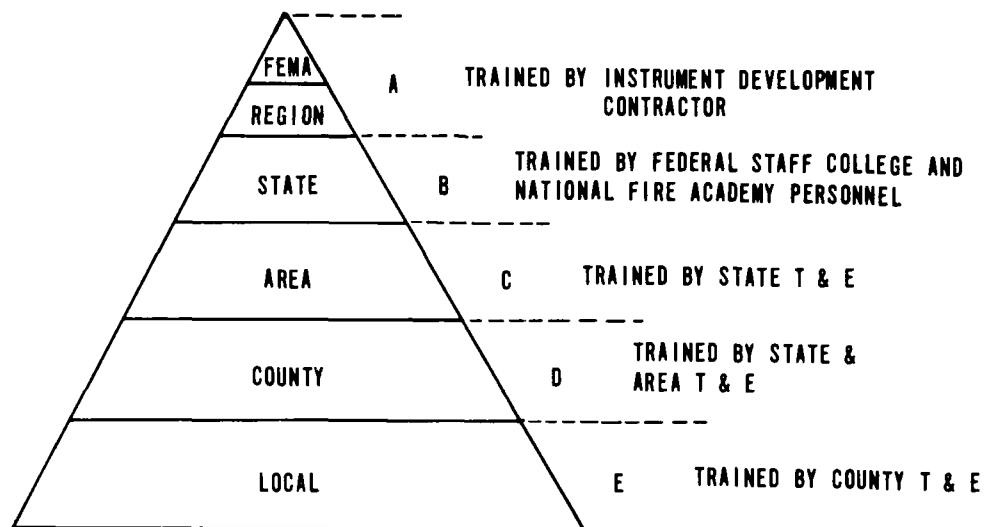
Although details of a training program would depend on the instrument type, some aspects of training strategy can be discussed at a general level. One possible training structure is outlined herein.

Upon completion of a viable detection/identification device that is completely operational, a training program should be instituted to develop individual skills in specialized emergency operational techniques. The training would be given to all persons identified by the organizations described in the preceding paragraphs as those who would be directly responsible for operating the equipment on the scene, or those who would be responsible for training others.

A formal training program can be accomplished by utilizing the existing training facilities of the various participating organizations. The initial thrust would be to develop a core group of trainers within each organization.

The structure of the former Defense Civil Preparedness Agency (now, FEMA) lends itself quite readily to utilization for training. There are ten (10) regions throughout the United States and territories, each of which has a Training and Education (T&E) officer. These persons are responsible for the Civil Defense educational effort within their respective regions.

At the next lower level, the states and territories within each region have a T&E officer who is responsible for the educational effort within that particular state or territory. Each succeeding lower level of Civil Defense or Emergency Management (area, county, local) has someone who is responsible for the T&E program within their jurisdiction. By training these persons, the ultimate goal of training those in the field will be greatly expedited. See Figure 8.1.



GROUP A - FEMA REPRESENTATIVES, FEDERAL STAFF COLLEGE STAFF, NATIONAL FIRE ACADEMY STAFF, T&E OFFICERS FROM EACH REGION.

GROUP B - T&E OFFICERS FROM EACH STATE AND TERRITORY.

GROUP C - T&E OFFICERS FROM EACH STATE.

GROUP D - COUNTY EM COORDINATORS (DIRECTORS).

GROUP E - LOCAL EM COORDINATORS (DIRECTORS).

- THE LOCAL COORDINATORS (DIRECTORS) WOULD THEN BE RESPONSIBLE FOR TRAINING THE PERSONNEL SUCH AS POLICE AND FIRE AND RESCUE GROUPS IN THEIR JURISDICTION.
- NEW STATE AND LOCAL POLICE CANDIDATES WOULD RECEIVE THEIR TRAINING FROM POLICE ACADEMIES.
- NEW FIRE AND RESCUE PERSONNEL WOULD RECEIVE THEIR TRAINING FROM NATIONAL OR STATE FIRE SCHOOLS.

Fig. 8.1 - Emergency Management Training Hierarchy

By utilizing the facilities at the Federal Staff College in Battlecreek, Michigan, and the National Fire Academy in Emmitsburg, Maryland, the instructional staffs at each facility can be trained in the use of hazardous material detection instruments. This core of trainers can then be used to train the individuals designated as trainers from each state and territory. This would include those from any or all of the organizations who would use such instruments. As persons are trained, they can then return to their own facility and train the next lower level. This method should greatly expedite the training of those in the field and create a better capability to protect the lives of the population in areas where incidents occur involving hazardous materials.

The actual training course content would be determined once the detector is developed, and would include accident and/or disaster scenarios for simulation purposes. The scenarios would include built-in decision making situations as well as hands-on use of the detector. The course could include training in sharpening the senses as aids in material identification. A manual for use during the training program would also be developed.

8.2 Summary of Conclusions and Recommendations

Summaries are given below in the order in which the principal topics are presented in the body of the report. Because recommendations for further development often proceed naturally from a statement of conclusions concerning the present status of technology, the "Conclusions" and "Recommendations" sections are not presented separately, but are integrated.

8.2.1 Instrumentation Needs

Present methods of identifying materials, principally indirect (e.g., reading placards and shipping papers, or contacting CHEMTREC) are inadequate.

Instruments which are in use now are of limited application (e.g., explosimeters, detector tubes).

Emergency workers expressed interest in and a desire for an instrument which could identify materials

remotely. The instrument, however, would have to be simple to operate and reliable. Priority was placed on identification over quantification.

8.2.2 Hazardous Materials List

- A list of 115 materials with significantly hazardous properties and having a high probability of being encountered in an accident was derived.
- Infrared spectra show that over 90% of the materials have the potential of being identified by an IR absorption system. Yet, since a few materials are not amenable to such a detection system, some technique to supplement an IR system would be desirable.
- A more definitive and extensive list of materials considered hazardous for FEMA missions should be derived. Statistics on amounts transported and on actual accidents would be factored into this derivation.

8.2.3 Remote Sensing Instrumentation

- No remote sensing instrument exists which is ready for use now in a portable configuration for detection of hazardous materials.
- A passive, remote IR absorption system, the XM21, now being developed by the U.S. Army for chemical warfare agent detection offers the best promise for near-term development and application to hazardous material detection.
- The XM21 system is itself still in the developmental stage. Therefore, further monitoring of the progress of this program should be performed by FEMA.
- The XM21 system is designed specifically for a group of organophosphate materials. Therefore, analysis and development of a microcomputer-based discrimination subsystem to allow identification of many hazardous materials should be carried out.

- Further analyses of the radiation characteristics of hazardous material "targets" should be carried out in support of remote instrument development. These studies should include the temperature characteristics of both burning and non-burning targets and studies of atmospheric transport and absorption.
- Most present laser systems developed for atmospheric monitoring are unsuitable for application to hazardous material detection. Problems include the following:
 - 1) Many systems are designed to measure concentrations of known constituents rather than identify unknown materials. Thus, many systems are limited in design principle to one or a few materials.
 - 2) Lasers, particularly those operating in the visible range, pose serious eye-hazard problems.
 - 3) Laser monitoring devices are usually sophisticated instrument systems requiring skilled operators. Even systems which have been made mobile are complex and bulky (van-sized).
 - 4) Tunable lasers which, in principle, offer greater versatility in detection do not presently operate over broad enough continuous ranges to make them practical for the many-unknown hazardous material problem.
- Of the possible laser-based systems, a Raman scattering system shows some promise for long-term development, though still posing the eye-hazard problem. Using a single-frequency laser, a Raman system has the potential to detect many materials. Mobile systems have been built, but have been bulky because high power is required to overcome small Raman scattering cross sections. Any future developments of Raman detection systems should be monitored.
- As research progresses in the development of microcomputer data handling systems and in tunable lasers, the long-term possibility of a differential scattering, tunable laser system exists. Research and developments in these areas should be monitored.

8.2.4 Non-Remote Instrumentation

- A number of direct sampling, portable, production-level instruments exist which can be used now for special jobs in hazardous material emergencies, or which show potential for general hazardous material identification. No instrument exists, however, which in its present state can be used in the field to identify a material out of a large number of possibilities.
- A dispersive IR absorption instrument shows the best potential for near-term development into a practical instrument for field use. Production models exist, but a microcomputer discrimination subsystem to allow identification of many materials needs to be developed; such development should be supported.
- A portable gas chromatograph/mass spectrometer (GC/MS) system based on space technology and intended specifically for hazardous material identification is in its early development stages. This effort should be monitored and perhaps supported by FEMA.
- Present portable gas chromatographs would be useful for the analysis of complex gaseous or vapor mixtures, but are not candidates for the primary identification role.
- Advances in the technology of extreme miniaturization of GC components should be monitored for possible applications to a future GC/MS instrument.
- Detector tube kits exist and, though cumbersome, could be used for the identification of many materials. Their principal use, however, would be in monitoring known materials. No significant development needs are projected for this type of instrument.
- Chemicals kits for water analysis exist and would have useful applications for spills in and near water.

- The development of a kit for the identification of unknown solids and non-volatile liquids should be pursued. This kit would be based on the existing Hazardous Materials Spills ID Kit, and would supplement a system for identifying gases and vapors.
- Portable instruments designed for limited groups of materials exist and are in use, especially for the detection of explosive and flammable gases and vapors. No significant development needs are projected in this area.
- A number of special-purpose instruments have been developed, or are being developed, for ancillary functions related to hazardous material emergency operations. Support in these areas would be of value, but is seen as secondary to the development of an instrument for primary identification of a hazardous material. See Section 6.2.6 for details on specific instrument functions.
- The value of the human senses as an aid in material identification should not be ignored. Training programs in the recognition of sensible characteristics of hazardous materials should form a part of the training of emergency workers.

8.2.5 Heat Source Detectors

- A number of portable IR detectors exist for identifying hot spots amid debris or smoke, or for measuring temperatures. A more widespread use of these instruments could be promoted, but no significant development needs are projected.

The evaluations conducted in this study have shown that the ideal instrument for the identification of hazardous materials is far from a reality. Particularly in the area of remote detection, the task of developing such an instrument is formidable. This study has, however, identified ongoing efforts and

existing techniques whose further development can lead to significant improvements in our capabilities for responding to hazardous material emergencies.

APPENDIX A

SURVEY OF EXPERIENCES OF EMERGENCY WORKERS
WITH HAZARDOUS MATERIAL ACCIDENTS

While one of the authors of this report was attending the NFPA Seminar "Handling Hazardous Materials Transportation Emergencies" at Allentown, PA, October 30 to November 1, 1979, he took a survey of the emergency workers attending the seminar. A questionnaire containing 15 questions relating to actual experiences and opinions was handed out to all participants. The results of this survey are summarized in the sections that follow.

The seminar was attended by emergency workers with a variety of backgrounds from the northeastern part of the U.S. Though the majority of participants were firefighters, there were also representatives from the police, industry, and various state or community organizations such as the PA Emergency Health Services Council. The experience of those attending ranged from people who had never seen a hazardous material accident before, to Fire Chiefs with over 25 years of experience fighting fires and hazardous material emergencies.

Of the approximately 50 questionnaires that were handed out, 31 responses were received. While this does not represent a large number in statistical terms, the answers given do represent a sizable body of information which is of value because it comes from the people who would use hazardous material instruments if they were developed. As research on instruments to be used for hazardous material emergencies proceeds, further and more extensive surveys of this nature would be valuable in assuring that development efforts proceed in line with actual needs and likely uses by those in the field.

In the discussion to follow, the questions asked in the actual survey will be repeated, and the responses will be summarized as concisely as possible. Where quantitative results or factual data are possible, they will be given. Some of the questions, however, were deliberately cast to elicit comments and opinions. In these cases, a verbal summary of the trend of the answers, with some representative quotations where appropriate, will be given. In some cases, those completing

the questionnaires chose not to answer a particular question, so the number of responses to each question is not always thirty-one.

1. Number of years' experience dealing with hazardous material emergencies.

<u>Years' Experience</u>	<u>No. of Replies</u>
0	6
1-5	8
6-10	5
11-20	4
over 20	4

2. Approximately how many hazardous material incidents have you dealt with or witnessed?

Answers varied from none, to very specific numbers, such as 4, or 7, to very approximate figures such as "50 or more." Taking into account estimates for the approximate figures, the experience of a total of about 400 hazardous material incidents is represented in the survey.

3. Can you list some or all of the specific materials that were involved in these incidents?

Answers included very specific chemical names as well as generic terms such as "hydrocarbons." The materials mentioned and the number of times they were listed are summarized below:

<u>Material Name</u>	<u>Number of Times Listed</u>
Hydrocarbon Fuels	9
Chlorine	8
LPG	6
Ammonia	5
Propane	5
Methyl Ethyl Ketone	4
Acids - various	3
Isopropanol	2
Sulfuric Acid	2
Picric Acid	2
Ployvinyl Chloride/Vinyl Chloride	2
Acrylonitrile	2
Natural Gas/LNG	2

<u>Material Name (Cont'd.)</u>	<u>Number of Times Listed</u>
Radioactive Materials	2
Fertilizers	1
Cellulose Nitrate	1
Acrolein	1
Mercaptan	1
Calcium Hypochlorite	1
Sodium Hyposulfite [sic]	1
Acetaldehyde	1
Styrene	1
Phenol	1
Carbon Disulfide	1
Ethylene	1
Paint Resins	1
Epichlorohydrin	1
Chloropicrin	1
Methoxychlor	1
Ethyl Alcohol	1
Parathion	1
Acetone	1
Dichloromethane	1
W.P. (White Phosphorous?)	1
Alcohol	1
Chloride	1
Pesticides	1
Herbicides	1
Class A Explosives	1
Class B Explosives	1
Class C Explosives	1

This list of materials can be compared to the list derived in Section 4 of the report. Of the 41 materials or groups listed in the survey, 35 are contained in, or have some component in, Table 4.1.

4. What methods have you used, or would you now use, to identify what hazardous material is present in an accident? If you use any specific instruments, perhaps you could briefly describe them and name the manufacturers.

Of the answers given, approximately 43% indicated that no instruments were used, but indirect methods, such as reading placards or shipping papers, or calling CHEMTREC, were used. A list of the specific instrument types mentioned by those who did indicate such a use follows:

Explosimeter
MSA Explosimeter
Davis Explosive Gas Tester
Gas Tester
Gas Detector
MSA Combustible Gas Indicator
Grace Industries Electronic Nose
MSA "Universal Tester"
Universal Test Kit and Tubes
Draeger Tubes
MSA CO Test Monitor
Probe-Eye
RADEF Monitors (radiation)
Victoreen, and other radiation meters

5. How often has a hazard identification placard or sign been visible? How often obscured or damaged beyond recognition?

Visible in approximately 67% of the incidents. Not visible in approximately 33% of the incidents.

6. How often has manifest information been easily available? How often difficult or impossible to obtain on a timely basis?

Available in approximately 48% of the incidents. Unavailable in approximately 52% of the incidents.

7. Can you state approximately what proportions of accidents involving hazardous materials were accompanied by fire or explosion, compared to those where no fire occurred?

Fire or Explosion: Approximately 28% of incidents.

No Fire or Explosion: Approximately 72% of incidents.

8. What do you see as the main drawbacks of an instrument which requires taking a sample of the material to be identified? Would such an instrument be useful at all?

The main concerns expressed were the expected ones of danger to the person taking the sample. As one responder

stated, "The present philosophy precludes approaching materials until they are known. What method can be devised to protect the sample collector?" Nevertheless, most felt that such instruments would be useful. Some of the other concerns expressed were accuracy and reliability of such an instrument, the time required to calibrate and use the instrument, and the need for proper training.

9. What would you see as possible drawbacks of an instrument which could remotely (say, from a distance of 500-2000 feet) identify a material?

Most agreed that such an instrument would be desirable and useful: "I'll take one now," and "very valuable." The main drawbacks people foresaw were the likely complexity of such an instrument, and hence the difficulty of training men to use it, and keeping them current, especially in volunteer companies. Concern was also expressed over cost, the time to get such an instrument to the site and use it, and its reliability and accuracy.

10. Could you comment on the relative importance of simply identifying what material is present compared to being able to quantitatively measure the amount of a material (e.g., in parts per million)?

Of those who responded to the question, all agreed that identifying the material would be the first priority. Measuring quantities, however, was seen as a valuable, though "secondary" input. Such information would serve to "modify actions" of the crew. "By knowing the amount, you could better regulate your suppression efforts."

11. One thinks of principal hazards in terms of dangerous gases or volatile liquids. Could you comment on the relative frequency of accidents involving non-volatile liquids or solids which are yet in some way hazardous?

Very few people had any inputs on this question. Of the few who responded, 3 had not experienced any incidents other than gases or volatile liquids; one mentioned several non-volatile acid spills; one mentioned that accidents with non-volatile liquids of solids occurred "much less often;" and one said they were "becoming more frequent."

12. Do you think there is a significant need for an instrument to test for explosive or flammable concentration of gases or vapors?

All but two of the respondents agreed on the value of such an instrument.

13. Do you think there would be a significant use for an instrument that could detect hot spots (and possibly cold spots) which are visually obscured, e.g., by smoke, or a wall?

Out of the total number of questionnaires returned, 20 agreed that there would be significant use for such an instrument; 2 felt that there would not be; 4 noted that such instruments were already available, with no other comment; and 5 did not respond.

14. Recognizing the immense technical difficulties of designing a lightweight, portable, easy-to-operate instrument which could identify any material, what would you see as your most pressing need in terms of a feasible instrument to use in hazardous material emergencies.

There were few responses to this question. Of those making specific suggestions, the following are excerpted: "speed in determination of the material due to possible exposure danger," "explosive level tester," "mobile lab," "flashpoint, decomposition point, shock sensitivity," "a placarding and labeling system far superior to the present one, properly enforced, not

only on the Federal level, but also on the State and local level," and more of "what we use now, i.e., CHEMTREC and hazardous materials books."

15. Use this space for any additional comments which you feel would be helpful, or for completing questions for which you need more room. In particular, are there any problem areas not covered in the preceding questions?

No one took advantage of this question to offer further comments.

APPENDIX B

PROJECTIONS OF REQUIREMENTS FOR A PORTABLE
RAMAN SYSTEM TO DETECT HAZARDOUS MATERIALS

In this appendix we have attempted to make a rough extrapolation of the applicability of a Raman system to incidents involving hazardous materials. We have not tried to consider the many engineering problems of adapting such a system to portable use, but have simply estimated some of the requirements, assuming such a system could be built. The estimates are based on projections from information on existing large systems.

Two aspects are significant: the resolvability or detectability of a wide range of materials by this method, and the beam intensities or energy outputs required.

H. Inaba has indicated the positions of principal lines in the Raman spectra of atmospheric constituents and common pollutants; this information is reproduced in Figure B1. The addition of major lines from the 115 hazardous materials discussed in Section 4 would considerably complicate this picture. However, the fact that the lines tend to be relatively well-separated gives some hope for the ability to potentially discriminate one material from another. Where a line from one material would coincide with that from another material, the likelihood of different secondary lines would allow discrimination. Though the intensities of lines present in Raman spectra differ from those in IR spectra, the whole question of detectability is very similar to that discussed in Section 4.2 with reference to IR spectra. One added advantage of Raman spectra, however, is that diatomic molecules such as C_2 and F_2 give significant Raman lines even though they are not infrared active.

Both Inaba, et al, and Block Engineering have made estimates of the minimum detectable concentrations of various substances. Inaba, et al, have calculated the detectable limits of SO_2 , making certain assumptions about laser system performance; these predictions are reproduced as Figure B2. Their predictions are complemented by experimental data on SO_2 gathered at nighttime with their mobile system (which used a pulsed Nd:YAG laser, but with different characteristics than those assumed in Figure B2). Though these measurements did not attempt to establish minimum detectable concentrations, one can infer from the

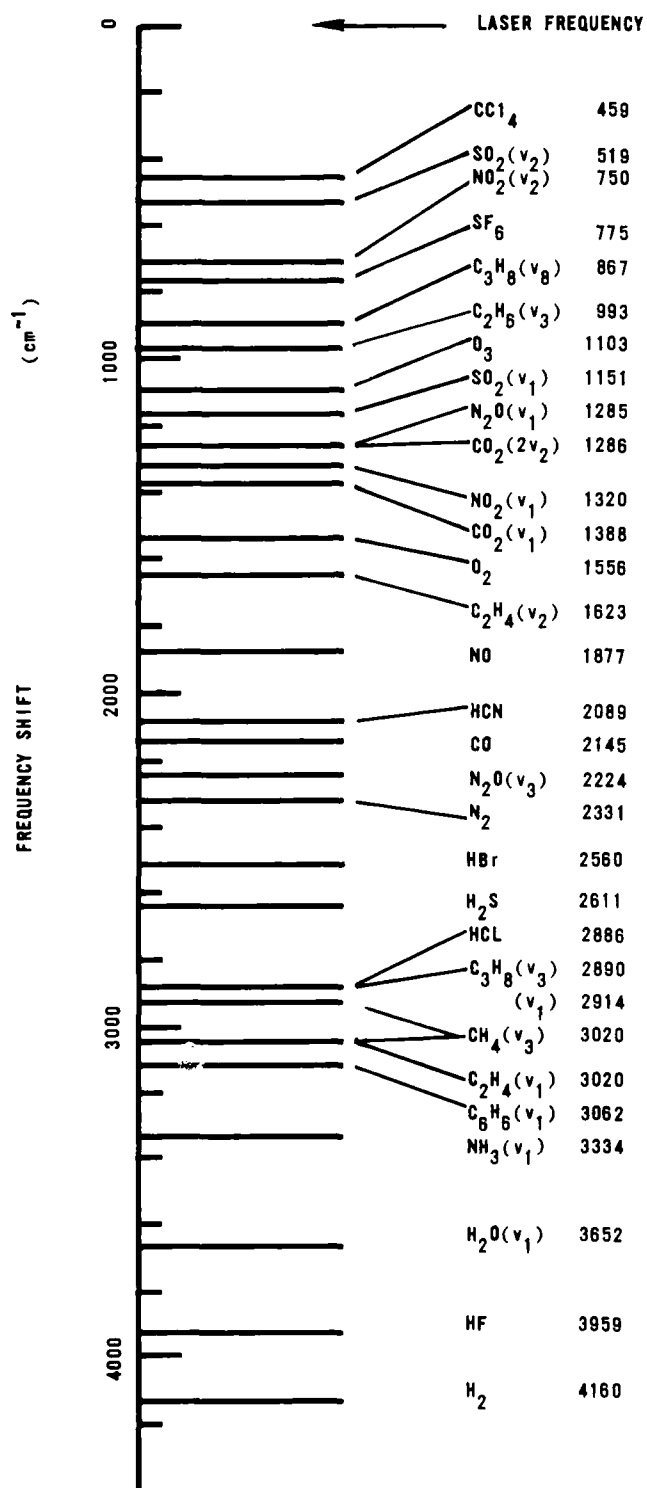


Fig. B1 - Frequency Shifts of Q-branch of Vibrational-Rotational Raman Spectra of Typical Molecules Present in Ordinary and Polluted Atmosphere Relative to the Exciting Laser Frequency (Reference 51, p. 159, used with permission)

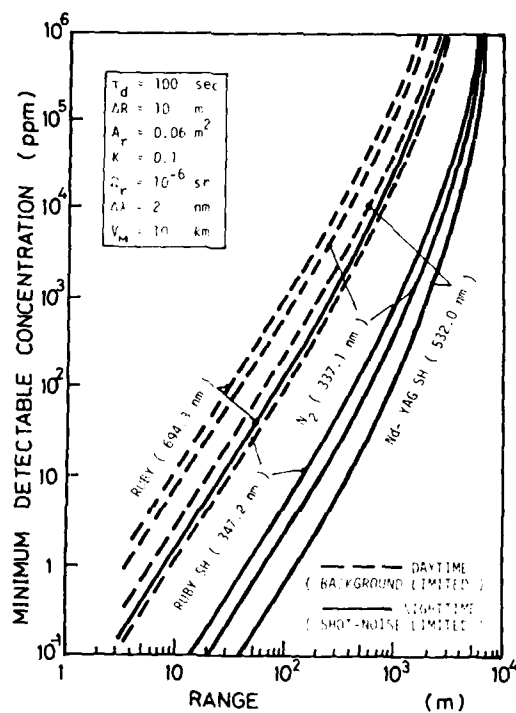


Fig. B2 - Analytical Comparison of Minimum Detectable Concentrations of SO₂ Molecules, as a Typical Example of Gaseous Air Pollutants, as a Function of Range for the Laser Radar System Utilizing Raman Scattering Scheme with Presently Available Laser Transmitters. (Reference 136, p.119, Used with Permission)

signal-to-noise values presented that the concentration of 1850 ppm which they sensed would have been initially distinguishable after about 1000 shots (52).

The group at Block Engineering has presented experimental data on air, water vapor, SO_2 , and kerosene; and with the help of this data, they have estimated the detection limits of a number of other materials as shown in Table B1. (Note that their list contains a number of potentially hazardous materials.) They show experimental data for the detection of 30 ppm of SO_2 at a range of 280 m and an observation time of 50 seconds. Their tabulated value of a limit of 8 ppm for the detection of SO_2 is presumably a correction for different signal-to-noise ratios, times, and ranges.

From the data mentioned above, it is possible to make some rough projections of the requirements for a hypothetical portable system. One can set certain constraints on the system and then extrapolate the output energy requirements for the laser source. The main difference between the mobile systems described above and a portable system for hazardous material detection would be the need for much smaller dimensions in the receiving optics, compensated for by the fact that one would likely be looking for much higher concentrations of the unknown materials. Let us assume that we would try to build a system with 10 cm diameter optics to detect minimum concentrations of one part per hundred of an unknown material. Since experimental data exist for both a second harmonic ruby laser and a second harmonic Nd:YAG laser, projections will be made for both types. The common material for which information exists, and for which projections will be made, is SO_2 .

Table B2 summarizes the system characteristics and detection limits for the two actual mobile systems, the theoretical predictions of Inaba, et al, and our hypothetical portable system. Making the very bold assumption that system characteristics such as optical efficiency and detection efficiency could be made the same for a smaller system, the energy requirements for a portable system have been extrapolated, based on each of the other systems, and are summarized in Table B3.

Table B1 - Predicted Detection Limits for the
Army/Block Engineering Mobile Remote Raman Spectrometer
(Reference 53a, with permission)

Compound	Detectable Concentration* (ppm)
Sulfur Dioxide	8
Nitric Oxide	56
Ammonia	8
Hydrogen Chloride	9
Hydrogen Sulfide	4
Hexane	1
Carbon Monoxide	25
Methane	4
Hydrogen	10
Benzene	2
Organic Phosphates	< 0.1
Nitrogen	24
Oxygen	17
Sulfur Hexafluoride	6
Aliphatic Hydrocarbons	< 3
Primary Amines	< 6

*The assumed signal-to-noise ratio is 5, the
time of observation is 20 seconds and the
range is 250 meters.

**Table B2-Characteristics of Actual and Hypothetical
Raman Systems for SO₂ Detection**

	Inaba et. al. Theoretical Nd: YAG		Inaba et. al. Mobile System		Inaba et. al. Theoretical Ruby		Army/ Block Engineering	Hypothetical Portable Nd: YAG	Hypothetical Portable Ruby
	Nd: YAG, SH	Nd: YAG, SH	Nd: YAG, SH	Nd: YAG, SH	Ruby, SH	Ruby, SH			
Laser Type									
Wavelength (nm)	532	532	532	532	347	347	Ruby, SH	Nd: YAG, SH	Ruby, SH
Pulse Energy (mJ/pulse)	30	30	4	4	50	50	2000	532	347
Pulse Rate (per sec)	100	100	40	40	1	1	2	40	2
Observation Time (sec)	100	100	~25	~25	100	100	20	100	100
Receiver Diameter (cm)			50	50			~90	10	10
Receiver Aperture. (m ²)			0.165	0.165	0.06	0.06	~ 0.64	0.008	0.008
Range (m)	200	200	228	228	200	200	250	200	200
Time of Operation	day	night	night	night	day	night	day		
Minimum Detectable Concentration (ppm)	1000	3	1850	1850	500	20	8	10,000	10,000

Table B3 - Projections of Pulse Energy Requirements for Hypothetical Portable Raman Systems

		PULSE ENERGY REQUIREMENTS (mJ)		
		Projections based on Inaba et al, Theoretical	Projection based on Inaba et al, Mobile System	Projection based on Army/Block Mobile System
Nd: YAG Second Harmonic System	Day	2.8	---	---
	Night	0.084	3.3	---
Ruby Second Harmonic System	Day	9.4	---	20
	Night	0.4	---	---

Note: These projections are based on the hypothetical system characteristics listed in the last two columns of Table B2.

Two observations can be made about the values shown in Table B3. First, the differences in energy requirements between daytime and nighttime operation are large. Obviously, any system designed for hazardous material accidents must be able to operate both day and night, so the higher energy requirements apply. Secondly, there are large differences between projections based on experimental data and on theory, with the higher requirements being shown for the actual systems. Though the system characteristics assumed by Inaba, et al, for their theoretical predictions are stated to be conservative, they apparently fall short of actual system applications.

Thus, for daytime operation, a portable laser Raman system in the tens of milliJoule range would seem to be required. While this is not an enormous energy requirement, and is achievable in the laboratory, it is significant for a portable system. The levels are high enough to make the eye hazard problem discussed earlier very real. As mentioned previously, the Army/Block Engineering System operating at 2 Joules per pulse was estimated to pose an eye hazard up to several kilometers. If we assume that the energy were reduced from 2 Joules to 2 milliJoules, then an eye hazard would exist at a range of about 30 to 40 meters. Whether such a condition would be acceptable in an operational system would have to be decided by the cognizant agency.

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DETACHABLE SUMMARY FOR
940 4
INSTRUMENTATION FOR DETECTING
HAZARDOUS MATERIALS
June 1980

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NOTE: The following summary is a reprint of the Executive Summary included as Section 1.0 in the main report. This detachable summary is included for the convenience of those readers who wish to have a brief synopsis of the report separable from the main contents.

DETACHABLE SUMMARY

Purpose and Scope

The purpose of this study has been to evaluate the state of material sensing technology and to analyze its relevance to FEMA missions in the area of hazardous material emergencies. For accomplishing this purpose, the following tasks were performed:

- A list of hazardous materials most likely to be encountered in FEMA emergency missions was compiled, along with pertinent data on these materials.
- An extensive survey of existing instruments and those under development was conducted; and their potential for hazardous material detection was evaluated.
- The requirements for future development of promising systems were determined.

In this study, emphasis has been placed on instruments which would be portable, easy to use, and suitable for the first emergency group to arrive at the scene of an accident. Within this emphasis, additional emphasis was given to remote instruments over those for which a sample of the material must be taken. Nevertheless, because of the number of direct-sampling instruments, a large portion of the report is devoted to these types. Though the study concentrated on instruments for immediate response, comments on the applicability of some systems to intermediate, and late-time response, are made where appropriate.

The emphasis has also been placed on instruments which could identify, out of a large number of possibilities, an unknown hazardous material. Less detail has been devoted to instruments applicable to limited numbers of materials or to functions other than detection and identification of unknowns.

List of Materials

Table 1 presents the names of the hazardous materials which were compiled to serve as the "target" list for the remainder of

Table 1 - Selected List of Hazardous Materials

GROUP I A

MATERIALS AMONG THE TOP 50 CHEMICALS PRODUCED
AND WHICH SHOW A SIGNIFICANT HAZARD

Sulfuric Acid	Propylene	Xylene	
Oxygen	Benzene	Hydrochloric Acid	Cyclohexane
Ammonia	Ethylene Dichloride	Ethylene Oxide	Acetone
Ethylene	Toluene	Ethylene Glycol	Propylene Oxide
Chlorine	Ethylbenzene	Ammonium Sulfate	Acrylonitrile
Sodium Hydroxide	Vinyl Chloride	Butadiene	Isopropyl Alcohol
Phosphoric Acid	Styrene	Cumene	Vinyl Acetate
Nitric Acid	Formaldehyde	Acetic Acid	Acetic Anhydride
Ammonium Nitrate	Methanol	Phenol	Ethanol

GROUP I B

PETROCHEMICAL OR OTHER FLAMMABLE PRODUCTS KNOWN TO BE SHIPPED
IN LARGE QUANTITIES AND HAVING A HIGH FLAMMABILITY RATING

Gasoline	Propane	Isobutane	Heptane
Kerosene & Jet Fuels	Butane	Pentane	Octane
Fuel Oils	Isopentane	Hexane	Natural Gas
Ethane			Acetylene

GROUP II

MATERIALS IN DEPARTMENT OF TRANSPORTATION'S SELECTED HAZARDOUS
MATERIALS GUIDE, AND WHICH ARE NOT ALREADY IN GROUP I

Acrolein	Epichlorohydrin	Hydrogen Fluoride	Methyl Ethyl Ether
Boron Trifluoride	Ethyl Chloride	Hydrogen Sulfide	Methyl Mercaptan
Bromine	Ethyleneimine	Methane	Nitrogen Tetroxide
Carbon Disulfide	Fluorine	Methylamines	Phosgene
Dimethyl Ether	Hydrogen	Methyl Bromide	Phosphorus Trichloride
Dimethyl Sulfate	Hydrogen Cyanide	Methyl Chloride	Sulfur Dioxide
	Titanium Tetrachloride		

GROUP III

MATERIALS PRODUCED IN QUANTITIES GREATER THAN 10⁸ LBS.
PER YEAR AND WHICH SHOW A SIGNIFICANT HAZARD

Chlorosulfonic Acid	Acetaldehyde	Methyl Methacrylate	Turpentine
Phosphorus Pentasulfide	Butenes	Aniline	Isopropyl Acetone
Acetone Cyanohydrin	Phosphorus	Butyl Alcohol	Ethyl Acetate
Isoprene	Carbon Tetrachloride	Potassium Hydroxide	Nonene
DDT	Napthalene	Trichloroethane	Chlorobenzene
Cyclic Rodenticides	Perchloroethylene	Ethanolamines	Chloroform
Cyclic Insecticides	N-Propyl Alcohol	Aluminum Fluoride	Barium Carbonate
Sulfur	Trichloroethylene	Perchloric Acid	Tetramethyl Lead
Calcium Fluoride	Tetraethyl Lead	Maleic Anhydride	Dichlorobenzene
Calcium Carbide	Methyl Ethyl Ketone	Sodium	Dinitro Aniline
	Ammonium Perchlorate		

the study. Further details on the derivation of the list are presented in Section 4.0. Data were collected on degree of hazard and on infrared spectra for these materials. Infrared spectra show that most (over 90%), but not all, of these materials should be identifiable by an IR absorption instrument system.

Promising Instrument Approaches

Sections 5.0, 6.0, and 7.0 of this report are devoted to a review of specific instrument types, with an emphasis on evaluating their applicability to hazardous material detection. Table 2 summarizes the principal instrument types evaluated, with brief comments on their status (a few instrument types which show little promise, or which serve functions other than detection are discussed in the body of the report, but omitted here). Those instruments with significant promise for future development are discussed briefly in the paragraphs that follow.

The development of a remote instrument to identify a hazardous material out of a large number of possibilities poses formidable problems, discussed at length in Section 5.0. To date, no known instrument which is capable of performing this function has reached the hardware stage. Designing and building such an instrument at the laboratory level would be a difficult task. Making such an instrument to be rugged, portable, and easy to operate is far more difficult yet.

The instrument type which holds the most promise for eventual application to multi-hazardous material detection would be a development of the U.S. Army XM21. This instrument is, itself, in the developmental stage, but it is designed for operation by a soldier in the field, and is thus to be rugged and portable. The instrument is intended for use with a relatively small group of organophosphate materials. Thus, the major development for hazardous material application beyond verifying that the Army model can perform as planned in field tests, is the design of a microcomputer-based discrimination subsystem. Further details on the present system and requirements for its application to hazardous material detection are given in Section 5.4.

Table 2 - Major Instrument Types Evaluated

Instrument Type	Reference Section	Remote/Non-Remote	Developmental Status	Comments
Passive IR Absorption	5.2.2.1, 5.4	remote	Developmental Stage	Potential for portable instrument, multi-material detection. Signal/Noise/Background problems can be significant. Development of U.S. Army XM21 system is most promising remote approach.
Active, Double-Ended Direct Absorption	5.2.1.1, 5.4	remote	Developmental/operational stage	A mobile van operational version exists. Possible adaptation of XM21 to this mode.
Laser Raman Scattering	5.2.1.3	remote	Developmental Stage	Multi-material capability; potential eye hazards; high power required. Large mobile versions have been built.
Laser Differential Absorption & Scattering	5.2.1.2	remote	Lab-type; operational	Many systems designed for single materials; multi-material systems at present very complex or limited in number of materials.
Correlation Spectroscopy	5.2.2.3, 6.2.1.1	remote or non-remote	Commercially available	Suited only for single material or small number of materials.
Non-Dispersive or Discrete Frequency Absorption	6.2.1.1	non-remote	Commercially available	Suited only for single material or small number of materials.
Dispersive Absorption	6.2.1.2	non-remote	Commercially available, but without discrimination subsystem	Potential for portable instrument, multi-material detection. Production models would require mainly development of discrimination subsystem.
Mass Spectroscopy or GC/MS combination	6.2.2, 6.2.4	non-remote	Developmental stage for portable version	Potential for portable instrument, multi-material detection.
Gas Chromatography	6.2.3	non-remote	Commercially available	Suitable for complex material separation, but not primary detection & identification.
Detector Tube Kits	6.2.5.1.1	non-remote	Commercially available	Available for many materials, but cumbersome where material identity is not known. Useful for monitoring known materials.
Chemical Kits	6.2.5.1.2, 6.2.5.1.3	non-remote	Developmental/operational stage	Useful for water analysis, analysis of solids or non-volatile liquids, or detecting general presence or absence of some hazardous material.
Combustible Gas Detectors	6.2.5.2.1	non-remote	Commercially available	Useful to monitor explosive or flammable concentrations, but not to identify materials.
IR Hot Spot Detectors	7.4	remote	Commercially available	Useful in various phases of firefighting.

If a detection instrument is not to operate remotely, but is able to perform some analysis on a sample of the material in question, the task is simplified somewhat. A large number of commercial and developmental instrument types are reviewed in Section 6.0. The instrument which shows the greatest potential for near-term development for hazardous material detection is a Dispersive Infrared Analyzer. Such instruments are commercially available in portable versions. As with a remote instrument, the aspect which needs development is a discrimination subsystem which would enable the instrument to compare a measured spectrum with data stored on many hazardous materials for quick identification.

The other non-remote instrument type which shows some promise for general hazardous material identification is a portable Gas Chromatograph/Mass Spectrometer. This instrument, described in Sections 6.2.2 and 6.2.4, is to be assembled from miniaturized components developed for spacecraft use. The present program is in its early stages; however, plans call for an emphasis specifically on hazardous materials, and include development of a computer data bank tie-in system.

With the emphasis on instrumentation, the potential of the human senses as an aid to material identification should not be overlooked. Training programs to help emergency personnel learn to recognize sensible manifestations of hazardous materials can be valuable and should be implemented.

Other techniques with more limited application or potential for development are commented on briefly in Table 2 and discussed at greater length in Sections 5.0, 6.0, and 7.0.

Recommended Actions

Detailed recommendations are contained throughout the report, and are summarized in Section 8.0. The following types of actions can be identified as important for FEMA in its role as responsible agency for hazardous material mitigation research:

- Support of programs to develop hazardous material detection instrumentation.

Depending on research funds available, the passive remote IR detection system and one or more of the possible

non-remote systems should be developed. The development of a non-remote instrument based on existing Dispersive IR Analyzers should be achievable within a year. Development time of a remote instrument is harder to predict, but because of the attractiveness of such a system, it should be supported with a high priority.

- Continuing monitoring of instrument development in areas related to hazardous material detection.

Because of the rapid progress in instrumentation technology, the continuing close monitoring of developments in related fields is important so that timely application to hazardous material detection can be made. Some specific areas (some of them overlapping) are IR detection technology, interferometer design, detector and cooling system technology, laser system applications, pollution monitoring programs, military chemical agent-detection programs, NASA-sponsored space exploration instrumentation development, and microcomputer data analysis applications.

Means of maintaining this monitoring function are close liaison with related programs and agencies, review of current literature, and attendance at key conferences such as the Bi-Annual National Conference on Control of Hazardous Material Spills and the Annual Symposium of the Society of Photo-Optical Instrumentation Engineers.

- Development of a definitive list of hazardous materials for FEMA missions.

Various agencies, e.g., EPA, the Department of Transportation, and the Coast Guard, have developed lists of materials defined as hazardous, according to criteria pertinent to their interests. Within the scope of time and funds available for this study, a list of materials posing significant hazards, and likely to be encountered in an accident, was compiled. However, a more definitive list based on more extensive statistical data can and should be developed.

- Support of programs to develop instrumentation for roles in hazardous material emergency operations other than identification.

Though the focus of this study was on instruments to identify an unknown material, instruments for other uses have been evaluated and commented on. Even if funds are limited, instrumentation needs for the entire range of response activities should be considered. Some specific types touched on in this report are alarms, personnel dosimeters or monitors, instruments for investigation of causes of accidents, and systems for obtaining material samples remotely or semi-remotely.

INSTRUMENTATION FOR DETECTING HAZARDOUS MATERIALS

Unclassified LOCUS, INC.
P.O. Box 740
State College, PA 16801
June 1980 246 Pages

Contract # DCPA01-79-C-0305 Work Unit # 2533-B

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